FINAL REPORT

Measurement and Computer Model Simulation of the Volatilization Flux
of Molinate and Methyl Parathion From a Flooded Rice Field

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ABSTRACT

This is a summary report for the 1985 rice field project conducted near Maxwell, California, to determine the volatilization rates (flux) of molinate (S-ethyl hexahydro-1H-azepine-1-carbothioate) and methyl parathion (0,0-dimethyl 0-p-nitrophenylphosphorothioate) from paddy water. Air samples, both high and low volume, along with water and soil samples were taken from May 18th through May 24th, 1985, for analysis. Vertical flux was determined by the aerodynamic method from the low volume air samples and meteorological data. The observed fluxes were compared with those predicted by the EXAMS (Exposure Analysis Modelling System) computer model, using the same parameters as in the field.

The half-life for decline of dissolved molinate in field water was 84 hr, corresponding to a loss of 45% in 72 hr. Most of this loss was by volatilization, based upon a semi-controlled experimental determination that 40% was lost from uncovered jars of rice field water while 10% was lost from covered jars in 72 hr. However, determination of volatilization flux by the aerodynamic method led to an estimated volatilization flux of only 0.082 kg/ha/12 hr day, or a loss of 0.58 kg (13% of the amount applied) in 7 days and thus less than 10% in 72 hr. Thus, flux determined in 1985 was far less than expected (and also less than determined in a less rigorous 1983 study) -- a finding which may indicate shortcomings in the aerodynamic method as it is commonly employed.

The half-life for decline of dissolved methyl parathion in field water was 44 hr. Only a very small portion of this was due to volatilization, which occurred at a rate of approximately 1/10th of that of molinate when account was made of differences in water concentration of the two chemicals. This is

keeping with expectations based upon the Henry's law constant, which for methyl parathion is approximately 1/10th that of molinate.
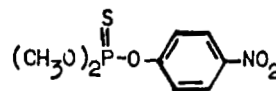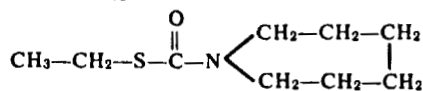
EXAMS was used successfully to model the diurnal variations in volatilization flux for both chemicals, by entering the appropriate physicochemical properties of the two compounds, field dimensions, and atmospheric conditions in the computer program. Water temperature and windspeed were the primary environmental determinants of volatilization flux, leading to maximum flux in late afternoon and early evening periods, when temperature and windspeed were at their maxima, and minimal flux during early morning periods. For molinate, EXAMS predicted approximately twice the rate of volatilization as was determined by the aerodynamic method, again supporting the contention of shortcomings in the aerodynamic method. EXAMS appeared to be quite promising as a predictive tool for estimating the rate of loss of chemicals from flooded rice fields by volatilization and other routes -- an area of much potential for further study.

This report contains detailed information on the sampling and analysis of rice field components, the application of the aerodynamic flux method, and the use of EXAMS.

INTRODUCTION

Volatilization represents a major loss route for many pesticides from agricultural field soil and water. Molinate, an important rice herbicide for post-emergent weed control in the Sacramento Valley, has physical properties (water solubility = 800 ppm, vapor pressure = 3.1×10^{-3} Torr, Henry's Law constant = 9.6×10^{-7} $M^3 \cdot atm/mole$, Table 1) suggesting that substantial loss by volatilization can occur in the first few days following treatment of a flooded rice field with herbicide granules. In 1983, we carried out the first

Table 1. Structures and Properties of Molinate
(Ordram) and Methyl Parathion

$$CH_3-CH_2-S-\overset{\overset{O}{\|}}{C}-N\underset{CH_2-CH_2-CH_2}{\overset{CH_2-CH_2-CH_2}{\diagdown}}$$

$$(CH_3O)_2\overset{\overset{S}{\|}}{P}-O-\overset{\hexagon}{}-NO_2$$

MOLINATE (ORDRAM)   METHYL PARATHION

Physical Properties

	MOLINATE	METHYL PARATHION
Molecular Weight	187	263
Water Solubility	800 ppm (20°)	37.7 ppm (22°)
Vapor Pressure	3.1×10^{-3} torr (20°)	1.1×10^{-5} torr (22°)
Henry's Law Constant	9.6×10^{-7} m^3·atm/mole	10.3×10^{-8} m^3·atm/mole

reported direct measurement of volatilization of molinate, using the aerodynamic flux method (Taylor, 1978), and observed 34% loss by volatilization in 4 days (Seiber et al., 1986; Ross et al., 1986). The observed flux correlated reasonably well with those predicted by the EXAMS computer model (Burns et al., 1981) through most of the sampling intervals. However, the experimental flux data from this experiment was not of high precision because we used only 2 rather than the recommended 6-8 sampling heights (Parmele et al., 1972) and thus were unable to determine the degree of adherence of our sampling results to those expected from aerodynamic theory. We also did not have frequent enough, or adequately representative water concentration data to allow for a precise normalization of our flux data to water concentration (ie $\mu g/cm^2/ppm$) -- an operation which is required in order to compare field-measured and EXAMS-calculated fluxes. We have thus essentially repeated the earlier experiment in order to obtain more precise flux measurements and better data for comparison of field-measured vs EXAMS-predicted flux.

Although unplanned, this second experiment also furnished an opportunity to obtain field flux data for methyl parathion -- a chemical applied several days before molinate to the same rice field for shrimp control. The physical properties of methyl parathion (S = 38 ppm, vp = 1.1×10^{-5} Torr, H = 1.03×10^{-7} atm$\cdot$m^3/mole, Table 1) also suggest that measureable losses will occur by volatilization from water, thus providing us with the opportunity to obtain measurements on a second chemical for further testing the predictive capability of EXAMS.

OBJECTIVES OF PROJECT

1. Measure the volatilization loss rate of molinate and methyl parathion from commercial rice fields.

2. Compare the field measured losses with those predicted by a computer model (EXAMS).

3. Refine the computer model based upon the field measurements and laboratory studies so that it can be used reliably to predict volatilization and other loss rates of pesticides applied to flooded rice fields.

EXPERIMENTAL

Field Study

A 23.6 acre (9.5 ha) rice pad in a ca 100 acre (40 ha) field, on the Gordon Wiley Ranch in Glenn County, was selected for its geometry with respect to the predicted prevailing winds and for its accessibility. A 18.5 x 0.3 m wooden pier was constructed on the west side of the pad approximately 170 m from the south side of the field. Some aspects of the experimental work are in Tables 2 and 3. A schematic diagram of the field is in Figure 1.

Low Volume Air Samples (Flux Samples)

The low volume sampling mast was placed on the south side of the end of the pier such that there would be little, if any, interference with the air fetch.* A piece of 1.2 cm dia by 1 m lab rack rod was driven into the clay and the mast clamped to the top. Air sampler cups were adjusted so that there

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* The rule of thumb for adequate Fetch is $\geq$ 100 m of treated surface on the upwind side of the sampling mast for a 1 m sampling height.

Table 2. List of Equipment Used for Field Study --
Molinate and Methyl Parathion Applied to Flooded Rice Field, 1985

1. Wind Profile Register system, model 104-LED-LM-DC
    CWT-1791 Thornthwaite and associates; Elmer, NJ

2. Microdatalogger Model CR-21X Campbell Scientific, Logan
    Utah

3. Temperature probe (flux and water), Model 107 Campbell
    Scientific, Logan, UT

4. High volume air samplers, Model U-1/AT, BGI, Inc., Waltham,
    MA

5. Generators, Honda Motor Co.

6. Ten junction thermopile for measuring change in
    temperature, D. E. Glotfelty (USDA Beltsville, MD)

7. Microflex Paristaltic pump, Cole-Parmer Instrument Co.
    Chicago, ILL.

8. pH Meter, Beckmann Scientific

9. C_{18} Bond elut, 5 ml size, Analytichem International, Harbor
    City, CA

10. Glass Fiber filters; 9 cm dia., Whatman # 934-AH,
    Fisher Scientific

11. XAD-4 Resin, Rohm and Hass Philadelphia, PA

12. Soil sampler, Arts Manufacturing and Supply, American
    Falls, Idaho

13. Low volume sampling cups (Gas dry hydrocarbon traps)
    Chemical Research Supplies, Inc, Addison Ill

14 Methanol, Acetone, Resi-grade, Baker Chemical Co.

15 Rotometer, model F-1500, Gilmont Instruments, Inc.
     Great Neck, NY

16 High volume air samplers, Bendix Co., Baltimore, MD

Table 3. Time Schedule of Events for Field Study; Molinate and Methyl Parathion Applied to Flooded Rice Field,1985

DATE	ACTIVITY
5/5/85	Furadan applied in a 70 ft. swath to borders
5/8/85	Field seeded with Foundation L202 seed
5/15/85	Pier constructed on west bank of pad; Methyl parathion applied
5/16/85	Anemometers calibrated
5/17/85	Background air, water and soil samples taken; Water sampling station markers set out
5/18/85	7:00-9:00 Background water sample taken; deposition samplers put in place 9:30-10:10 Field applied with molinate 10:20-24:00 Flux, upwind air, downwind air, water and soil samples taken
5/19/85	00:00-19:45 Flux, upwind air, water and soil samples taken 7:45-9:30 Molinate applied to field located directly to south of field
5/20/85	06:00-20:00 Flux, upwind air, water and soil samples taken
5/22/85	06:00-20:00 Flux, upwind air, water and soil samples taken 07:20-08:00 Methyl parathion applied to field directly to the south
5/24/85	06:00-20:00 Flux, upwind, water and soil samples taken

Figure 1. Schematic Diagram of Rice Field -- 1985 Study
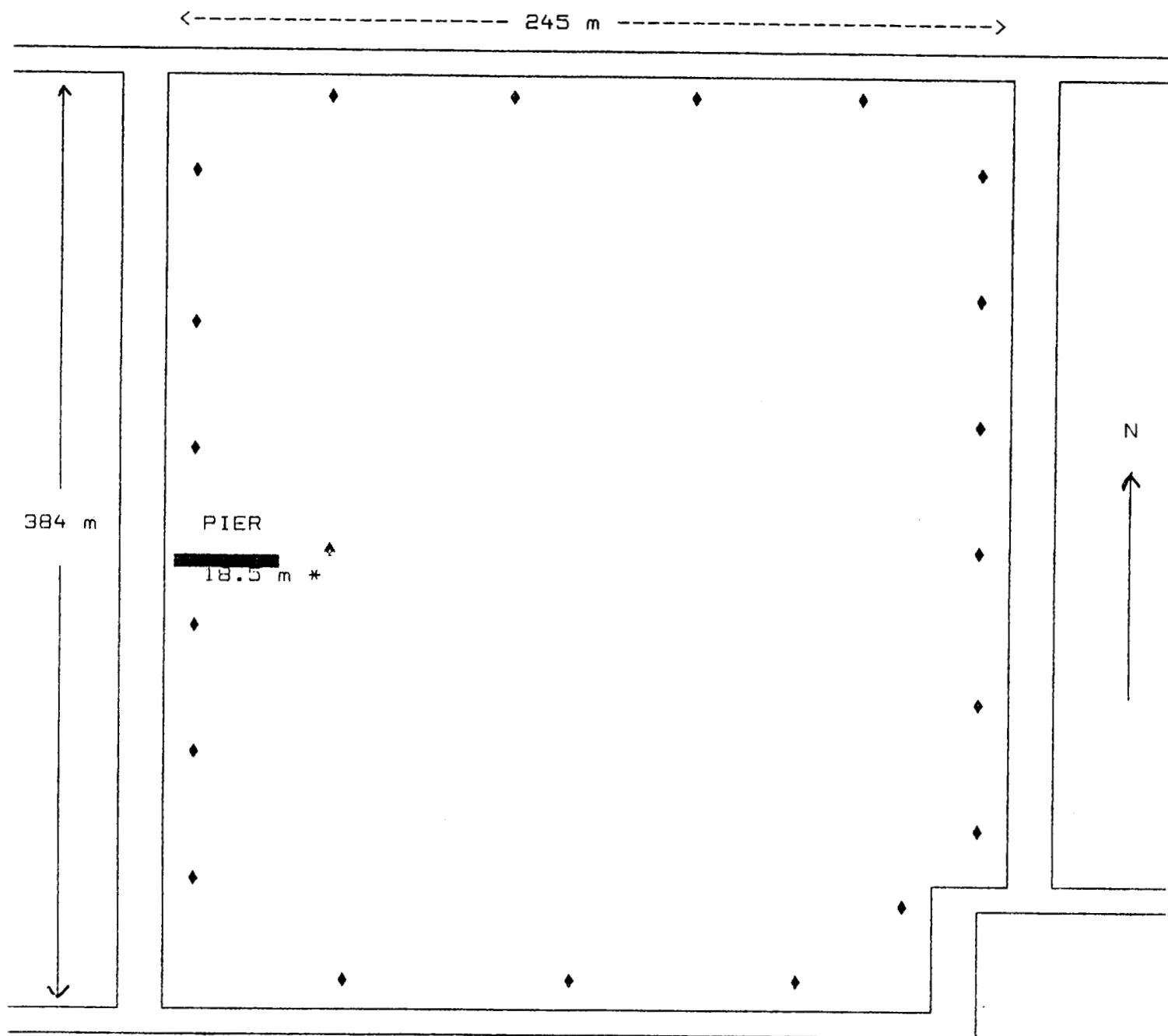
♦ Water and Soil Sampling Station
♠ Meteorology Station
* Air Sampling Staion

was a logarithmic progression of sampling heights that consisted of sampling points at 20, 30, 50, 80, 125 and 200 cm above the water. Sampling cups, 3.2 cm i.d. by 12.6 cm in length, were made by cutting aluminum gas drying cylinders in half. A 100 mesh screen was placed in the bottom of each cup. XAD-4 resin (40 ml), a 20-50 mesh macroreticular resin, was placed in each sampling cup. Three sampling cups were connected to a high volume air sampling pump via Tygon tubing (1 cm i.d. x 1 mm wall x 1.25 cm o.d.). The pump was modified with a three port manifold that allowed an air flow rate of approximately 50 liters per minute through each sampler.

Air flow rates were measured at the beginning of each sampling period by attaching a rotometer via Tygon tubing and a rubber stopper to the entrance of each sampling cup. The rotometer reading was noted and the flow rate in liters/minute was calculated by using the empirical calibration equation 0.86 x reading - 1.2. Total air volumes were calculated from the flow rate multiplied by the length of the sampling period.

Meteorological Instrumentation

Six anemometers were attached to a 3 cm diameter by 3 m pole that was located 8 m east of the end of the pier. The anemometer heights were adjusted to form a logarithmic pattern. The anemometers were calibrated prior to field experimentation, by positioning all on a horizontal line directly into the wind in such a way that there was no influence of one anemometer to another.

Also located on the meteorological mast was an apparatus measuring differential temperature (del T) consisting of a ten junction thermopile that was shielded and aspirated. The temperature sensors were located

approximately 25 and 64 cm above the water surface; these heights determined the flux plane. The reading accuracy was 0.02 degrees centigrade. The water temperature (water T) and flux plane temperature (flux T) probes were also attached to the mast. The probes were accurate to ± 0.2°C. Cables extended from the meteorological mast back to the end of the pier and to the control center where the del T, water T and flux T were interfaced into a micrologger.

The micrologger collected data every three seconds, and summed and averaged over 15 min periods. The 15 min average data were downloaded in the laboratory onto an IBM PC via a tape recorder each day. Further data reduction was done utilizing both the data base and spread sheet programs, dBase II and Lotus 123 respectively.

Wind direction apparatus was set up near the data receiving center (a wooden cabinet containing microloggers and receivers) and the wind was measured continuously, at a height of 1.8 m, for the duration of the experiment.

Water Samples

Twenty water sampling stations were set up at 50 m intervals around the edges of the paddy. Stakes that were marked with 5 cm divisions were driven 3 m from the paddy edge into the sediment until 40 cm remained from the surface to the top mark. The depth of the water was read by taking the reading of the water level and subtracting from 40 cm. The level of the water was recorded during each water sampling period.

Water samples were taken from shore using a 3 m aluminum pole that had a 500 ml glass container attached. Approximately 150 ml of water (3 scoops of 50 ml each) was sampled at each station. At each station, one scoop (50 ml) was placed into one of three large glass containers, yielding 3 replicate

composites for each sampling interval. Each replicate (1000 ml) was filtered immediately through a glass fiber filter to remove floating particulate matter. C_{18} Bond eluts were rinsed once with 2 ml of Resi-grade methanol then twice with 3 ml of distilled water. Filtered rice water (100 ml) was passed through the Bond elut at a flow rate of 15 ml/min via a peristaltic pump. The eluts were then rinsed with ca 3 ml of distilled water then placed in a jar and frozen at -20°C until time of analysis.

Soil Samples

Two or three composite soil samples were taken each day of sampling (Table 2). The composited samples consisted of one soil core (10 x 10 cm) taken at each water sampling station. The sample was mixed in a tub, then a 500 gram subsample was filtered using a Buchner funnel to filter off any excess water. The sample was transferred to a Mason jar and then placed on dry ice until transferred to the lab where it was kept frozen (-20°C) until analyzed.

The soil samples were suction-filtered through a Buchner filter to remove excess water. They were then air dried for 1 day. Samples not used for analysis were baked in an oven (112°, overnight) to obtain the dry weight upon which the analytical data were based. These air-dried samples (50 g each) were extracted with 2 x 250 ml of 20% diethyl ether/methylene chloride in a Polytron type apparatus. The extract was then filtered, concentrated to a known volume, and analyzed by gas chromatography.

When control soil (3 portions) was spiked at 1.0 ppm with molinate, recoveries were 99.7, 103.7, and 84.0%, yielding an average recovery of 95.8%.

Deposition Rate

The deposition of molinate formulation was measured by placing 5 empty coffee cans on the west check of the field. Seven Dixie cups were also placed on the west dike while ten were placed on the east dike. The deposition samplers were collected after the application had been complete. The coffee can and Dixie cup samples were kept separate. The contents of each were weighed upon return to the lab. From the weights, areas of the collector openings, and stated application rate of molinate, the application efficiency was calculated to have been 88%.

Application of Molinate

Molinate, 10 G, 40 lbs/acre (10% a.i.), was applied on May 18th between 9:30 and 10:05 am by a commercial applicator (Jade Flying Service, Williams). The plane flew in an east-west direction. High volume samplers were placed at the downwind and upwind edges of the field and were running during and after completion of spraying. Low volume flux sampling began ten minutes after completion of application.

Analysis of Water

The Bond elut was allowed to come to room temperature (ca 1 hour) before extraction. The eluts were placed in a 15 ml glass centrifuge tube and 2 ml of Resi-grade ethyl acetate was added to each elut. The tubes were spun using a lab centrifuge for one minute. After spinning, the top layer was drawn off and 1 ml of ethyl acetate was again added to the elut. The elut apparently holds ca 0.5 ml of residual water from the sample itself. The centrifuge extraction procedure needs at least 4 x 1 ml of ethyl acetate to achieve complete extraction.

Analysis of XAD-4 Resin from High and Low Volume Air Samples

For low volume samples, 90 ml of ethyl acetate was added to each XAD resin sample in a 250 ml Erlenmeyer flask and then swirled for 30 minutes. The solvent was decanted and filtered through Whatman number one filter paper into a 500 ml sample storage container. Fresh solvent (60 ml) was added to the flask and then swirled for 15 minutes. The solvent was then transferred and another portion of solvent (50 ml) was added and the flask was swirled once more for 10 minutes. For high volume samples, the initial volume of ethyl acetate was 150 ml while successive aliquots were 100 ml. The size of the flask was 500 ml. Samples were concentrated using a Kuderna Danish apparatus to approximately 6 ml. Further reduction of solvent, if necessary, was accomplished using a micro 3-ball Snyder column. Samples were first analyzed for molinate then methyl parathion.

Recovery Experiments

Water samples -- A 1000 ml sample of field water having a molinate concentration of 14 ppb was spiked at 1.0 ppm and stirred for 1 hour. An aliquot (100 ml) was passed tnrough a Bond elut and then eluted with ethyl acetate. Three replicates were taken yielding a recovery average of 96.6%, with a standard deviation of 1.7%.

Because of the already high concentration of methyl parathion in the rice water, no recovery experiments could be performed. However, other investigators have obtained recoveries in the 90% range for methyl parathion in rice water using bond eluts.

Freezer spike -- Six samples of 100 ml each of water 0.33 ppm in molinate was Bond eluted. Three Bond eluts were analyzed immediately while the other

three were placed in the freezer (-20°C) for two months. The per cent

difference was ca 8.1%. No freezer stability studies were done for methyl

parathion.

Resin samples -- Recovery was 92% when resin was spiked with 10

micrograms of molinate, and 81% when spiked with 1 microgram.

Trapping efficiency for resin:

When air was spiked with 100 micrograms for two hours with a flow rate of

50 ml per minute (6 m^3 of air passing through the resin) recoveries averaged

78% with s=2.3 (n=3). We previously determined that methyl parathion was

recovered with >70% efficiency under similar conditions (Woodrow and Seiber,

1978).

Jar Experiments for Estimating Molinate Loss Paths in Field

To each of 20 1- quart Mason jars was added sediment (From 5-18-85

sampling of Ordram paddy) to a depth of 1 inch. Then enough field water,

first enriched by mixing with Ordram granules (sufficient to give an estimate

of 1-2 ppm of molinate in solution), was added to give about a 5 inch depth

over the sediment. The jars were loaded at 1400 on 5-19-85 then covered with

aluminum foil and lids. They were then inmersed in mud near the shore of the

paddy.

At 1200-1230 on 5-20-85, 10 jars were designated open (no lids) and 10

were designated closed (lids). From each set of 10 jars, a composite sample

was taken by withdrawing 2 ml of water from each jar of the set, and mixing

the resulting 20 ml in a sample jar. The sample jar was sealed with an

aluminum foil liner in the lid, labelled, and frozen.

After sampling, the Mason jars were again inmersed in water-sediment near

the dike of an adjacent paddy. Sampling was done periodically in this manner

for up to 222 hr.

Gas Chromatography

Molinate was analyzed on a Hewlett Packard 5710A gas chromatograph with a nitrogen-phosphorous detector. The column was a 30 meter x 0.31 mm DB-1 WCOT fused silica capillary with a .25 micron film thickness. Flows for nitrogen, air and hydrogen gases were 1.5, 50 and 3 ml/min, respectively. The split ratio was approximately 59:1. Temperatures for injector, column and detector were 250, 150 and 250°C, respectively.

A Tracor MT-220 gas chromatograph with a flame photometric detector and a phosphorous filter (526 nm) was used for methyl parathion analysis. A Hewlett Packard 3390A integrator was attached to filter the signal, thus increasing sensitivity. The column was a 1.5 m x 3 mm 1.95% OV-17, 1.5% QF-1 on 80-100 mesh Chrom W HP. Flow rates, in ml/min, for nitrogen (carrier), air, and hydrogen were 55, 80 and 60, respectively.

Calculation of Flux

The vertical flux was calculated using the following equations:

$$R_1 = \frac{g}{T} \frac{\left(\frac{t_2-t_1}{z_2-z_1} + \Gamma\right)}{\left(\frac{U_2-U_1}{z_2-z_1}\right)^2} \qquad \text{Eq. (1)}$$

$$\emptyset = (1 \pm 16Ri)^{\pm 0.33} \qquad \text{Eq. (2)}$$

$$P = \frac{K^2(C_1-C_2)\,(U_2-U_1)}{\left[\log\left(\frac{z_2-z_o}{z_1-z_o}\right)\right]^2 \emptyset^2} \qquad \text{Eq. (3)}$$

where:

    C is the pesticide concentration in air at heights Z_1 and Z_2

    T is the temperature in degrees K

    Z is the vertical height; Z_2= height of upper probe of delta temp

        apparatus; Z_1 = height of lower probe of delta temp apparatus; Z_0

        = roughness height and = 0 for water

    Γ is the dry adiabatic lapse rate: = 9.86 E-5 K/cm

    g is the acceleration due to gravity

    U is the wind speed in cm/sec at the flux heights Z_1 and Z_2

    R_i is the Richardson Number and may be positive or negative (+

        indicates stable conditions while - is unstable and zero is

        neutral)

    P is the vertical flux at the geometric means of the two heights Z_1

and Z_2

    K is the Von Karmon constant and is generally accepted to be 0.4

    ϕ is the atmospheric stability parameter

    t is the temperature in °C

RESULTS AND DISCUSSION

Water Samples

    Molinate was applied as granules (10% a.i.) to the rice paddy water at
the rate of 4.48 kg/ha a.i. Thirteen periods were used for water sampling,
with each period resulting in collection of 3 replicate composites taken from
2-3 m into the paddy from sampling stations evenly spaced around the field
perimeter. The results of each replicate are in Table 4, while Table 5 gives
averages for each sampling interval along with the water pH and depth. A

Table 4. Water Sample Concentrations
Molinate and Methyl Parathion

DATE	TIME	REP	MOLINATE PPM			METHYL PARATHION PPB		
			Individ.	Avg	(S)	Indiv	Avg	(S)
5-18-85	0815	—	0.014					
5-18-85	1100	1	1.24			189		
5-18-85	1100	2	0.91	1.04	(0.17)	135	153	(31)
5-18-85	1100	3	0.98			135		
5-18-85	1440-1630	1	1.96			120		
5-18-85	1440-1630	2	1.93	1.99	(0.09)	135	130	(9)
5-18-85	1440-1630	3	2.09			136		
5-18-85	1845-2000	1	2.15			129		
5-18-85	1845-2000	2	2.05	2.06	(0.09)	123	125	(3)
5-18-85	1845-2000	3	1.98			125		
5-19-85	0200-0430	1	2.43			110		
5-19-85	0200-0430	2	2.45	2.45	(0.02)	117	114	(4)
5-19-85	0200-0430	3	2.46			117		
5-19-85	1000-1040	1	2.34			106		
5-19-85	1000-1040	2	2.42	2.37	(0.05)	107	104	(3.8)
5-19-85	1000-1040	3	2.34			100		
5-19-85	1300-1330	1	1.75			94.9		
5-19-85	1300-1330	2	1.96	1.87	(0.11)	102	107	(17)
5-19-85	1300-1330	3	1.91			127		
5-19-85	1630-1700	1	2.14			85.1		
5-19-85	1630-1700	2	2.14	2.08	(0.10)	91.4	86.5	(4.4)
5-19-85	1630-1700	3	1.97			83		
5-20-85	0930-1015	1	1.72			68.1		
5-20-85	0930-1015	2	1.84	1.81	(0.08)	66.4	66.8	(1.1)
5-20-85	0930-1015	3	1.88			66		
5-20-85	1345-1415	1	1.79			57.6		
5-20-85	1345-1415	2	1.82	1.81	(0.02)	67	63.8	(5.4)
5-20-85	1345-1415	3	1.83			67		
5-22-85	0810-0850	1	1.26			46.7		
5-22-85	0810-0850	2	1.31	1.29	(0.03)	45.6	44.3	(3.1)
5-22-85	0810-0850	3	1.31			40.8		
5-22-85	1400-1430	1	1.20			36.7		
5-22-85	1400-1430	2	1.21	1.21	(0.01)	38.3	38.6	(2.1)
5-22-85	1400-1430	3	1.22			40.8		
5-24-85	0920-1000	1	0.96			12.5		
5-24-85	0920-1000	2	0.98	0.98	(0.02)	12.9	13.0	(0.61)
5-24-85	0920-1000	3	1.00			13.7		
5-24-85	1330-1415	1	0.941			11.9		
5-24-85	1330-1415	2	0.959	0.94	(0.03)	12.5	12.3	(0.42)
5-24-85	1330-1415	3	0.908			12.7		

Table 5. Average Concentrations, Standard Deviations, pH and
Depth for Water Samples — — Molinate and Methyl Parathion

TIME(Hr) (POST-APP.)	MOLINATE (PPM)		METHYL PARATHION (PPB)		pH	DEPTH cm
	AVE.	STD.	AVE.	STD.		
1.0	1.04	0.17	153	31	7.5	15.8
6.5	1.99	0.09	130	9.0	7.6	15.9
9.0	2.06	0.09	125	3.0	7.4	16.4
17.0	2.45	0.02	114	4.0	7.4	----
24.0	2.37	0.05	104	3.8	7.0	15.8
27.0	1.87	0.11	107	17	7.1	·15.5
30.7	2.08	0.10	86.5	4.4	6.9	15.2
48.0	1.81	0.08	66.8	1.1	6.7	14.7
51.8	1.81	0.02	63.8	5.4	6.8	14.4
94.0	1.29	0.03	44.3	3.1	6.6	14.0
100.5	1.21	0.01	38.6	2.1	6.6	13.8
144.0	0.98	0.02	13.0	0.61	6.7	13.6
148.0	0.94	0.03	12.3	0.42	6.6	13.8

background water sample taken just before application showed negligable (0.014 ppm) molinate in the paddy water. The origin of this background molinate is not known, although it could have been introduced in irrigation water used to flood the paddy, in drift from treatment of nearby fields, or from partitioning of molinate from the field atmosphere.

The concentration-time profile (Figure 2 and 3) showed an increase in molinate concentration to a maximum of 2.45 ppm at 17 hr after application, reflecting the time for dissolution of the granules. Approximately first order decline occurred thereafter, to ca 1 ppm 148 hr after application ($t^{1}/_{2} \cong$ 99 hr by linear regression of data points starting at 17 hr). The rate of decline was similar to that observed in a 1983 study (Seiber et al., 1986).

Methyl parathion was applied as an emulsifiable concentrate to the field 3 days before molinate, at an unknown rate. The sampling periods were the same as for molinate, that is, they began 3 days after the application of methyl parathion and thus cover the hours 72-206 after application of methyl parathion. Table 5 and Figures 4 and 5 present the data for the methyl parathion water concentration profile during that period, but referenced to the time of molinate application as time = 0. Decline was approximately first order, with a $t^{1}/_{2}$ of ca 44 hr. There are several $t^{1}/_{2}$ values given in the literature for methyl parathion hydrolysis in pure water:

Heath, 1956 50,200 hr (pH 8, 25°C)

Smith et al., 1978 2,333 (pH 8.5, 22°C)

Even though these values disagree markedly, they are both considerably higher than our observed dissipation half life of 35-40 hr (~pH 7, ~27°C). Because our flux data will show (below) that volatilization is a negligable process

Figure 2. Plot of Molinate Concentration <u>vs</u> Time in Rice Paddy Water.
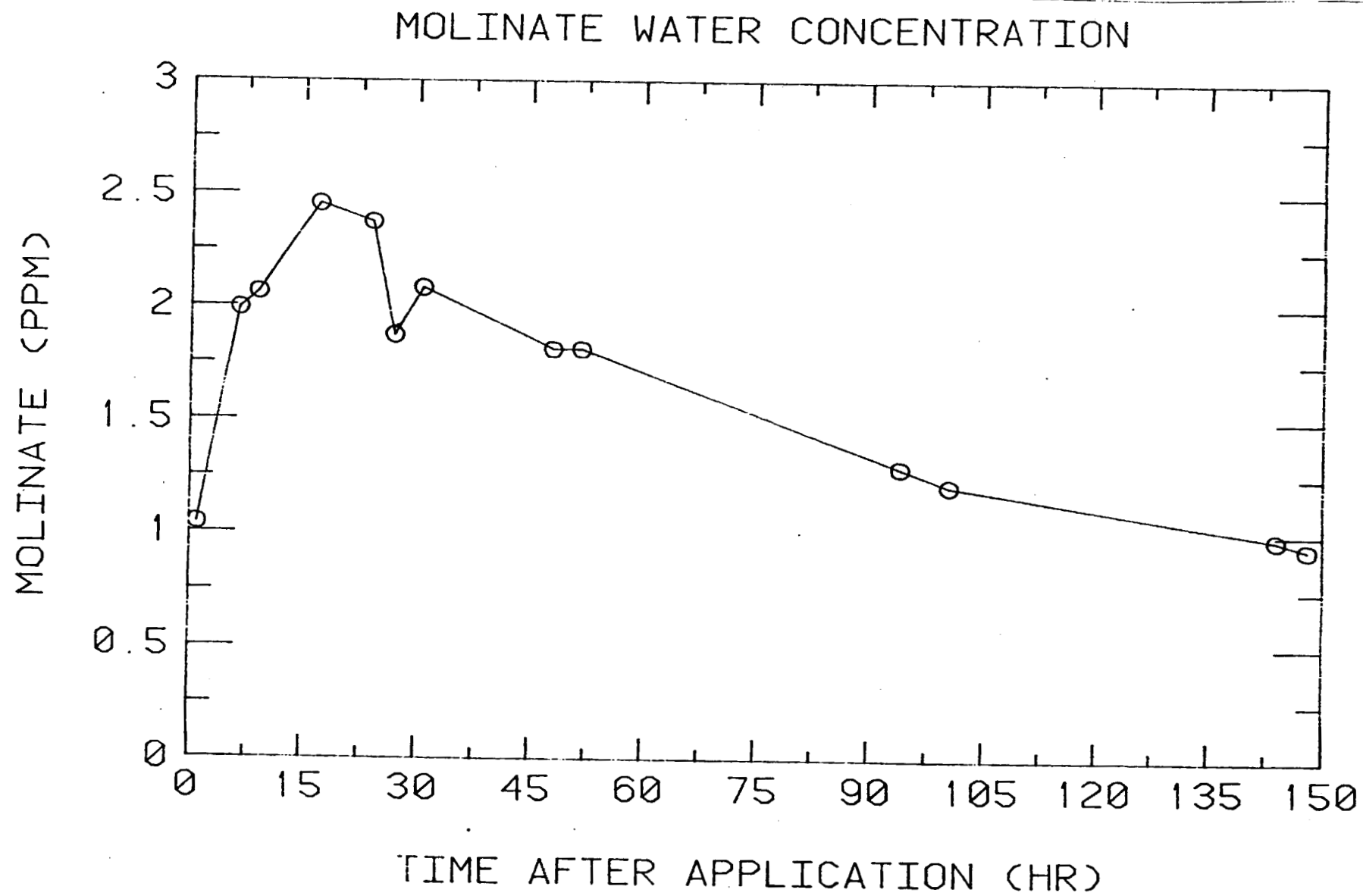

MOLINATE WATER CONCENTRATION

Figure 3. Plot of log molinate concentration vs time in rice paddy water. Best fit line starts with data point at 17 hr post-application.

METHYL PARATHION WATER CONC.
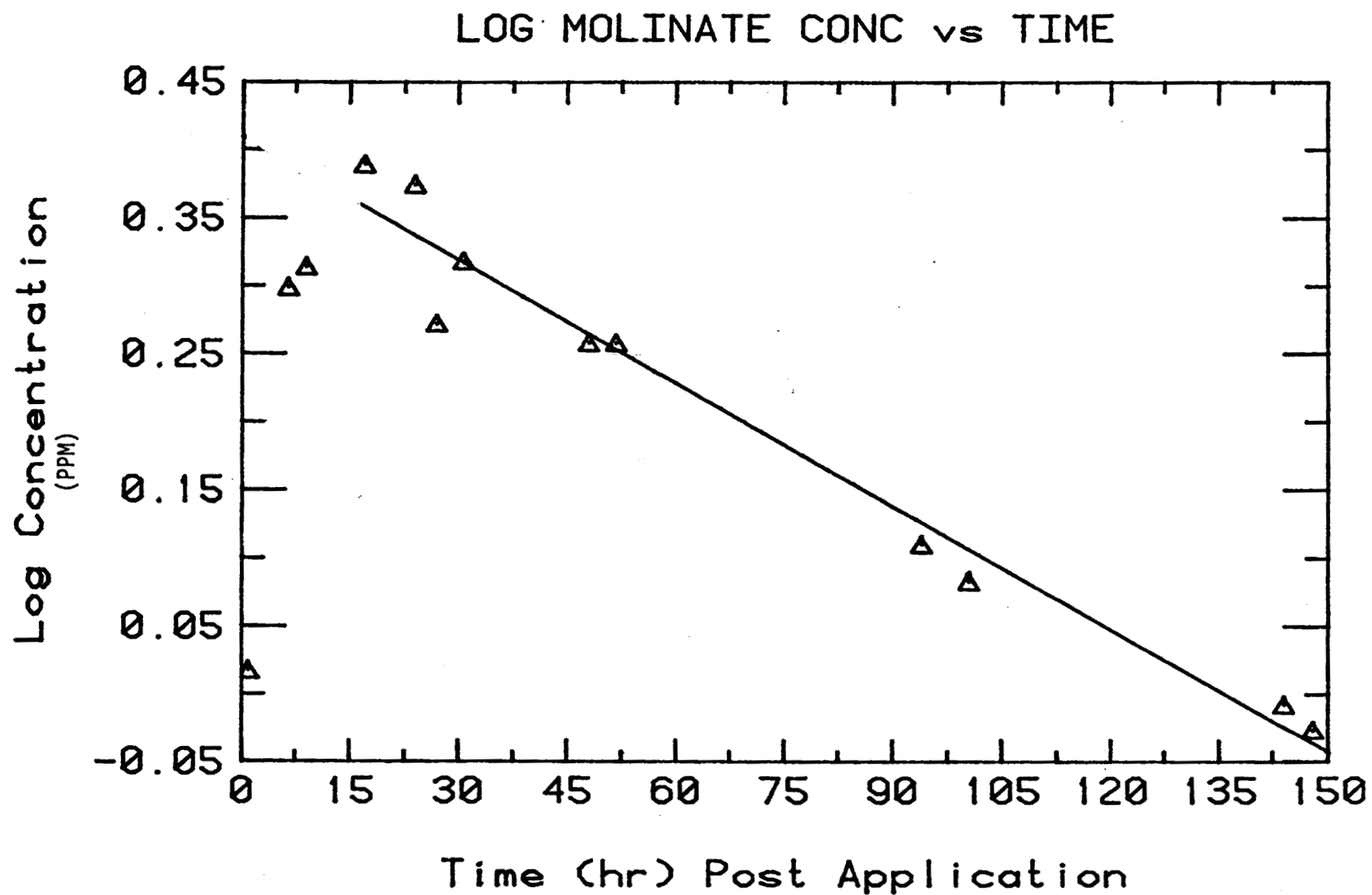
Figure 5. Plot of log methyl parathion concentration vs time in rice paddy water.

LOG METHYL PARATHION CONC vs TIME

T 1/2 = 44.3 hr

Log Concentration (PPB)

Time (hr) Post Application
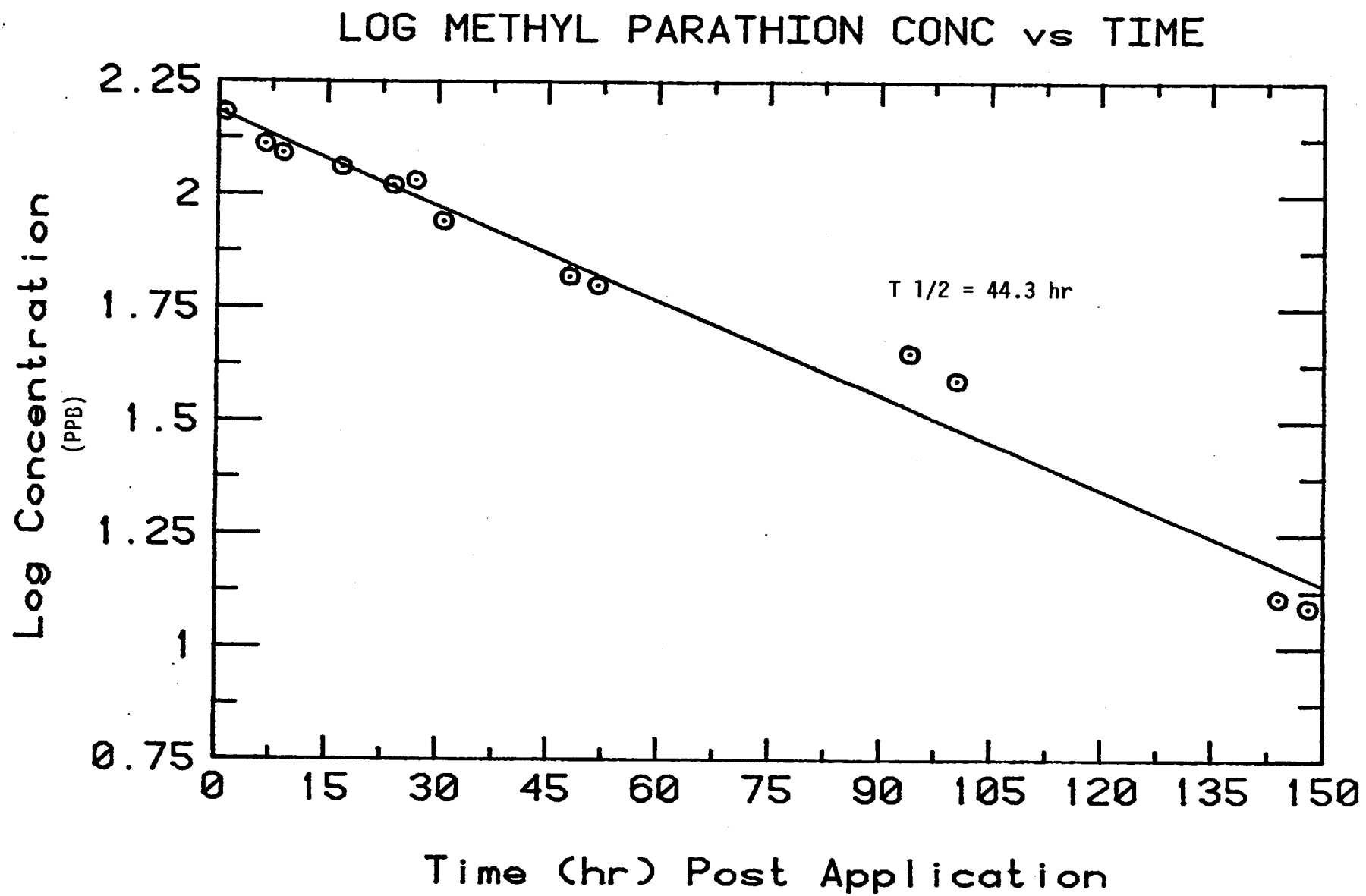
for methyl parathion dissipation, in keeping with the chemical's low Henry's law constant, we assume that a microbial or photochemical process is at least partly responsible for methyl parathion dissipation.

Soil Samples

The results from analysis of soil samples are given in Table 6. There was a very low content of molinate in background or control soil prior to application (0.015 ppm). The values for soils taken after treatment varied irregularly, yielding the highest value (0.55 ppm) on the last date of soil sampling (May 22, 1985). This variation is probably due to the poor sampling techniques employed; when a core of soil was raised through the overlying water, some surface material invariably washed off and some of the deeper core soil dropped out the bottom of the coring device. It is clear that a better technique is needed for sampling sediments reproducibly. It is worth noting that a previous molinate field sampling study showed an increase in molinate soil concentration with time (Ross and Sava, 1986) -- a finding also ascribed to sampling difficulties.

Air Sampling and Flux Measurements

Sampling was begun 10 min after the completion of the application of molinate and continued with 1 hr sampling periods with 15 min off to recharge the low volume samplers and refuel the generators. At midnight, and continuing until 19:45 the next day, May 19th, the sampling periods were increased to 2 hr intervals with 0.5 hr off. Days two, four and six (May 20, 22 and 24 respectively) each had five 2 hr sampling intervals with 1 hr off in between.

Table 6. Results of Molinate Analysis in Field Soil Samples.
All Results are on a Dry Weight Basis.

Sampling Date	Replicate	Conc (ppm)	Avg Conc (ppm)
5-17-85 (background)	1	0.013	
	2	0.0135	0.0151
	3	0.019	
5-18-85	1	0.379	0.379
5-19-85	1	0.152	
	2	0.170	0.161
5-20-85	1	0.202	
	2	0.192	0.197
5-22-85	1	0.555	
	2	0.538	0.547

The exact heights of the low volume samplers along with the anemometers and del T heights must be known accurately for flux calculations. Therefore, the depth of water in the field was monitored by reading a meter stick that was placed in the water near the pier, and the anemometers and sampler heights were adjusted accordingly (Table 7, see also code for sampling period in Table 8). Irrigation water was added to the field for a period of time just prior to the application of molinate until the next morning. The estimated flow rate into the field was 0.13 cubic meters per second. Evaporation and seepage was estimated at an average rate of 8.8 mm per day during day 1 through the morning of day 4. The rice plants began to break through the water surface on day 4 and more water was applied to "stretch out the plants."

Upwind high volume air samples indicated that there was no significant influx of molinate during the duration of the experiment (Table 9). The field directly to the south was applied with molinate on the morning of day one. The concentration found in the upwind (South) air sample during application was approximately one tenth of the concentration found at the same height at the low volume flux samplers, and thus was neglected in the calculations.

Table 7. Heights of Anemometers and Low Volume Air Samplers

PERIOD	ANEMOMETER HEIGHTS (cm)							LOW VOLUME HEIGHTS (cm)					
	A	B	C	D	E	F		A	B	C	D	E	F
1A	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
1B	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
1C	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
1D	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
1E	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
1F	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
1G	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
1H	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
1I	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
1J	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
1K	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
2A	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
2B	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
2C	19	34	53	88	149	250	:	16.5	26.5	46.5	76.2	121.5	196.5
2D	20	35	54	89	150	251	:	17	27	47	77	122	197
2E	20	35	54	89	150	251	:	17	27	47	77	122	197
2F	20	35	54	89	150	251	:	17	27	47	77	122	197
2G	20	35	54	89	150	251	:	17	27	47	77	122	197
2H	20	35	54	89	150	251	:	17	27	47	77	122	197
3A	20.5	35.5	54.5	89.5	150.5	251.5	:	17.5	27.5	47.5	77.5	122.5	197.5
3B	20.5	35.5	54.5	89.5	150.5	251.5	:	17.5	27.5	47.5	77.5	122.5	197.5
3C	20.5	35.5	54.5	89.5	150.5	251.5	:	17.5	27.5	47.5	77.5	122.5	197.5
3D	20.5	35.5	54.5	89.5	150.5	251.5	:	17.5	27.5	47.5	77.5	122.5	197.5
3E	21	36	55	90	151	252	:	18	28	48	78	123	198
4A	22	37	56	91	152	253	:	19	29	49	79	124	199
4B	22	37	56	91	152	253	:	19	29	49	79	124	199
4C	22	37	56	91	152	253	:	19	29	49	79	124	199
4D	22	37	56	91	152	253	:	19	29	49	79	124	199
4E	21.5	36.5	55.5	90.5	151.5	252.5	:	19.5	29.5	49.5	79.5	124.5	199.5
5A	21.5	36.5	55.5	90.5	151.5	252.5	:	19.5	29.5	49.5	79.5	124.5	199.5
5B	21.5	36.5	55.5	90.5	151.5	252.5	:	19.5	29.5	49.5	79.5	124.5	199.5
5C	21.5	36.5	55.5	90.5	151.5	252.5	:	19.5	29.5	49.5	79.5	124.5	199.5
5D	21.5	36.5	55.5	90.5	151.5	252.5	:	19.5	29.5	49.5	79.5	124.5	199.5
5E	21.5	36.5	55.5	90.5	151.5	252.5	:	19.5	29.5	49.5	79.5	124.5	199.5

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Table 8. Date, Time and Codes for Sampling Periods

PERIOD CODE	DATE	TIME START	TIME STOP	TIME AFTER APPLICATION (hr)
1A	5/18/85	10:15	11:15	0.75
1B	5/18/85	11:30	12:30	2.0
1C	5/18/85	12:45	13:45	3.3
1D	5/18/85	14:00	15:00	4.5
1E	5/18/85	15:15	16:15	5.75
1F	5/18/85	16:30	17:30	7.0
1G	5/18/85	17:45	18:45	8.25
1H	5/18/85	19:00	20:00	9.5
1I	5/18/85	20:15	21:15	10.7
1J	5/18/85	21:30	22:30	12.0
1K	5/18/85	23:00	01:00	14.0
2A	5/19/85	01:30	03:30	16.5
2B	5/19/85	04:00	06:00	19.0
2C	5/19/85	06:30	08:30	21.5
2D	5/19/85	09:00	11:00	24.0
2E	5/19/85	11:30	13:30	26.5
2F	5/19/85	14:00	16:00	29.0
2G	5/19/85	16:30	18:30	31.5
2H	5/19/85	19:00	20:45	34.0
3A	5/20/85	07:00	09:00	46.0
3B	5/20/85	09:45	11:45	48.8
3C	5/20/85	12:15	14:15	51.3
3D	5/20/85	15:45	17:45	54.8
3E	5/20/85	18:00	20:00	57.0
4A	5/22/85	06:00	08:00	92.0
4B	5/22/85	09:00	11:00	95.0
4C	5/22/85	13:00	15:00	99.0
4D	5/22/85	15:15	17:15	101
4E	5/22/85	18:00	20:00	104
5A	5/24/85	06:00	08:00	141
5B	5/24/85	09:15	11:15	144
5C	5/24/85	12:00	14:00	147
5D	5/24/85	15:00	17:00	150
5E	5/24/85	18:00	20:00	153

Table 9. HIGH VOLUME AIR SAMPLE RESULTS FOR MOLINATE AND METHYL
PARATHION

DATE	TIME ON	TIME OFF	AIR CONCENTRATION ($\mu g/m^3$)		SAMPLE TYPE
			MOLINATE	METHYL PARATHION	
5/18/85	----	----	0.0000	0.0000	BLK
5/18/85	08:00	09:30	0.50	0.0411	BG
5/18/85	09:38	10:22	11.30	0.0368	DW
5/18/85	10:19	11:43	1.86	0.0489	UW
5/18/85	10:24	11:35	3.34	0.0210	DW
5/18/85	11:38	12:57	4.69	0.0352	DW
5/18/85	11:47	12:52	2.95	0.0444	UW
5/18/85	12:54	14:12	1.12	0.0594	UW
5/18/85	13:00	14:19	4.53	0.0421	DW
5/18/85	14:14	16:53	0.471	0.0397	UW
5/18/85	14:20	16:47	7.82	0.0500	DW
5/18/85	17:09	19:36	0.353	0.0477	UW
5/19/85	08:00	10:10	0.424	0.0299	UW
5/19/85	11:50	13:10	0.0994	0.0411	UW
5/19/85	14:50	16:30	0.281	0.0151	UW
5/20/85	10:02	11:14	0.321	0.0105	UW
5/20/85	15:30	16:30	1.54	0.0182	UW
5/22/85	08:40	10:16	0.371	1.0300	UW
5/22/85	14:20	15:45	0.120	1.1600	UW
5/24/85	07:45	09:30	0.877	0.0505	UW
5/24/85	14:30	16:00	0.193	0.0483	UW

BLK = RESIN BLANK; BG = BACKGROUND;
DW = DOWNWIND; UW = UPWIND

note: Molinate was applied on the adjacent field on
5/19/85 and Methyl parathion on 5/22/85

Table 10. Water and Air Temperature Data for Flux Periods

DATE	TIME ON	TIME OFF	DELTA TEMP	WATER TEMP	FLUX[A] TEMP
5/18/85	10:15	11:15	-0.183	20.2	20.3
5/18/85	11:30	12:30	-0.137	22.7	25.0
5/18/85	12:45	13:45	-0.103	26.1	27.0
5/18/85	14:00	15:00	-0.188	28.9	31.3
5/18/85	15:15	16:15	-0.240	30.5	33.0
5/18/85	16:30	17:30	-0.086	31.3	30.0
5/18/85	17:45	18:45	-0.172	30.5	32.8
5/18/85	19:00	20:00	-0.122	28.4	29.5
5/18/85	20:15	21:15	-0.073	26.1	24.7
5/18/85	21:30	22:30	-0.084	24.3	22.4
5/18/85	23:00	01:00	-0.197	22.5	19.5
5/19/85	01:30	03:30	-0.180	20.5	17.6
5/19/85	04:00	06:00	-0.186	18.6	15.1
5/19/85	06:30	08:30	-0.105	18.0	16.4
5/19/85	09:00	11:00	-0.195	21.1	20.9
5/19/85	11:30	13:30	-0.131	26.9	26.1
5/19/85	14:00	16:00	-0.244	31.5	31.6
5/19/85	16:30	18:30	-0.141	31.4	33.0
5/19/85	19:00	20:45	-0.069	26.8	28.8
5/20/85	07:00	09:00	-0.084	17.2	17.4
5/20/85	09:45	11:45	-0.145	22.5	22.6
5/20/85	12:15	14:15	-0.104	28.6	29.3
5/20/85	15:45	17:45	-0.180	32.7	35.3
5/20/85	18:00	20:00	-0.126	30.9	30.8
5/22/85	06:00	08:00	-0.119	20.0	18.0
5/22/85	09:00	11:00	-0.127	22.9	23.3
5/22/85	13:00	15:00	-0.070	31.9	32.3
5/22/85	15:15	17:15	-0.102	33.7	35.1
5/22/85	18:00	20:00	0.120	29.9	32.4
5/24/85	06:00	08:00	-0.092	18.2	15.7
5/24/85	09:15	11:15	-0.094	23.2	23.1
5/24/85	12:00	14:00	-0.129	30.5	29.0
5/24/85	15:00	17:00	-0.257	34.4	32.8
5/24/85	18:00	20:00	-0.069	29.9	29.9

A: The air temperature at the height of the flux plane

Table 11. Anemometer Counts at Six Heights, and Anemometer Correction Factors

DATE	TIME ON	TIME OFF	A	B	C	D	E	F
5/18/85	10:15	11:15	3357	3563	3682	3803	3814	3927
5/18/85	11:30	12:30	3601	3806	3893	4011	2809	2880
5/18/85	12:45	13:45	2823	2948	3033	3131	2429	2514
5/18/85	14:00	15:00	3335	3502	3604	3708	3675	3860
5/18/85	15:15	16:15	3288	3473	3605	3725	3717	3872
5/18/85	16:30	17:30	4482	4758	4926	5088	5083	5037
5/18/85	17:45	18:45	5896	6344	6618	6875	6591	6846
5/18/85	19:00	20:00	6949	7554	7933	8279	8423	8699
5/18/85	20:15	21:15	7161	7800	8183	8545	8669	8996
5/18/85	21:30	22:30	3936	4226	4389	4504	4520	
5/18/85	23:00	01:00	6494	6949	7169	7387	7183	7268
5/19/85	01:30	03:30	9315	10059	10470	10814	10734	11039
5/19/85	04:00	06:00	5268	5508	5709	5745	4947	6009
5/19/85	06:30	08:30	5528	5678	5963	6068		
5/19/85	09:00	11:00	9664	10401	10880	11288	11464	11836
5/19/85	11:30	13:30	7795	8332	8657	8922	9010	9309
5/19/85	14:00	16:00	9587	10278	10672	11006	11112	11463
5/19/85	16:30	18:30	12896	13923	14514	15098	15300	15616
5/19/85	19:00	20:45	9853	10552	11013	11463	11476	11830
5/20/85	07:00	09:00	4650	5057	5206	5416	5445	
5/20/85	09:45	11:45	11937	13026	13496	14102		
5/20/85	12:15	14:15	7914	8471	8665	9027	8506	9494
5/20/85	15:45	17:45	.6224	6622	6701	7013	7069	7323
5/20/85	18:00	20:00	8391	9033	9172	9497	9466	9739
5/22/85	06:00	08:00	10031	11144	11289	11586	11424	12129
5/22/85	09:00	11:00	9892	10913	11212	11517	11568	12361
5/22/85	13:00	15:00	10018	10918	11214	11474	11433	11822
5/22/85	15:15	17:15	14157	15511	16090	16602	16546	17541
5/22/85	18:00	20:00	18768	20750	21722	22695	22981	24356
5/24/85	06:00	08:00	3147	3355	3481	3561		
5/24/85	09:15	11:15	4696	5040	5155	5308	5102	5505
5/24/85	12:00	14:00	8174	8802	9028	9394	9178	9852
5/24/85	15:00	17:00	11074	11961	12227	12875	12685	13510
5/24/85	18:00	20:00	19401	21203	22004	23323	13303	24555

CORRECTION FACTORS FOR ANEMOMETERS

ANEMOMETER HEIGHT	A	B	C	D	E	F
CORRECTION FACTOR	1.011	0.998	1.000	1.006	1.047	1.047

The field directly to the south was applied with methyl parathion on day four approximately half way through the first sampling period. The influx of methyl parathion into the field was far greater than the quantity that was evaporating off the field (Table 9). Therefore, vertical flux could not be determined for the duration of that day. The upwind high volume air samplers indicated that there was a 100-fold increase in concentration over the prior day's sample.

Table 10 contains the average differential, water and air temperatures for each period of flux sampling.

Wind speed in cm/sec was calculated from the anemometer counts (Table 11) divided by the period, in minutes, times the anemometer correction factor, and the steady state calibration equation:

$$U = 11.490 + 2.5767*C - 0.000448*C^2 + 0.00000028730*C^3$$

where C is the corrected counts per minute and U is the wind speed in cm/sec. From this value wind speed was calculated in cm/sec.

In general, the wind was from the southeast or south and gained in force as the days progressed. At night calm conditions occurred and the wind shifted to the west or southwest during the early morning hours. The size of the field gave more than adequate fetch; the accepted rule is that for every unit in height of sampling there should be 100 units of fetch -- a condition more than satisfied in this field situation.

The water and air temperatures generally were very similar (Table 10), but showed the expected lag in the late mornings when the air warmed more rapidly than the water, and in the night time, when the water held its heat longer than the air.

The flux plane was determined by finding the geometric mean of the two heights (the square root of Z_1 times Z_2). The flux plane varied slightly with time due to the addition of water to the field on days zero and six, as well as to evaporation and seepage losses. Pesticide concentration for heights Z_1 and Z_2 were obtained by a best fit plot of the observed pesticide concentrations against log Z. The wind speed at heights Z_1 and Z_2 were determined from the anemometer data in the same way (cf Table 12).

The wind speed profiles were reasonably linear with the exception of the last day of sampling, May 24th. Apparently the counter for the anemometers at the two upper-most heights was erratic; therefore, the wind speed profiles for those periods were plotted using the lower four anemometers.

The molinate concentration profiles were, for the most part, linear with height (See example in Figure 6). However, the concentrations at either extreme, 20 and 200 cm, varied to some degree (Table 13). Some periods, usually when the wind had a westerly component, gave profiles that were curved rather than linear at the 125 and 200 cm sampling points. This could be attributed to "edge effects" or to the fetch being less than ideal.

Vertical Flux was calculated from Equation 3. Flux values for molinate (Table 14) are presented graphically in Figure 7. The trend was towards minimum flux in early morning (at approximately 4-7 am on the day after application) and maximum flux in early evening (4-7 pm on days 1, 2, and 3 after application). For days 5 and 7 sampling was discontinued in the evening before it could clearly be determined when the maximum occurred, although even for those two days the highest flux values recorded were at 3 - 5 pm. The flux maxima for the five days ranged from 69 (day 7) to 198 $ng/cm^2/hr$ (day 5). The flux profile (Figure 7) is discontinuous reflecting the fact that no measurements at all were made on days 4 and 6, and that only daylight sampling was done on days 3, 5, and 7.

Table 12. Meteorological Data used for Flux Calculations

DATE	TIME ON	TIME OFF	HEIGHTS Z_1	Z2	DELTA TEMP	AIR TEMP	WIND U_2	WIND U_1
5/18/85	10:15	11:15	25.0	62.5	-0.18	20.3	170.2	157.6
5/18/85	11:30	12:30	25.0	62.5	-0.14	25.0	178.6	169.5
5/18/85	12:45	13:45	25.0	62.5	-0.10	27.0	142.2	133.7
5/18/85	14:00	15:00	25.0	62.5	-0.19	31.3	166.0	157.1
5/18/85	15:15	16:15	21.5	59.0	-0.24	33.0	165.4	154.4
5/18/85	16:30	17:30	21.5	59.0	-0.09	30.0	221.0	206.0
5/18/85	17:45	18:45	21.5	59.0	-0.17	32.8	291.8	265.1
5/18/85	19:00	20:00	21.5	59.0	-0.12	29.5	347.2	310.6
5/18/85	20:15	21:15	21.5	59.0	-0.07	24.7	357.2	321.6
5/18/85	21:30	22:30	21.5	59.0	-0.08	22.4	198.0	181.5
5/18/85	23:00	01:00	21.5	59.0	-0.20	19.5	315.3	297.4
5/19/85	01:30	03:30	22.0	59.5	-0.18	17.6	234.0	212.5
5/19/85	04:00	06:00	22.0	59.5	-0.18	15.1	134.2	121.8
5/19/85	06:30	08:30	22.0	59.5	-0.11	16.4	140.2	131.3
5/19/85	09:00	11:00	22.0	59.5	-0.20	20.9	244.3	222.0
5/19/85	11:30	13:30	22.0	59.5	-0.13	26.1	195.9	180.8
5/19/85	14:00	16:00	22.0	59.5	-0.24	31.6	237.3	218.4
5/19/85	16:30	18:30	22.0	59.5	-0.14	33.0	319.8	290.1
5/19/85	19:00	20:45	22.5	60.0	-0.07	28.8	246.3	224.3
5/20/85	07:00	09:00	22.5	60.0	-0.08	17.4	123.4	112.8
5/20/85	09:45	11:45	22.5	60.0	-0.15	22.6	298.4	268.5
5/20/85	12:15	14:15	22.5	60.0	-0.10	29.3	198.3	183.2
5/20/85	15:45	17:45	22.5	60.0	-0.18	35.3	158.0	146.6
5/20/85	18:00	20:00	23.0	60.5	-0.13	30.8	207.7	193.0
5/22/85	06:00	08:00	24.0	61.5	-0.12	18.0	251.0	228.4
5/22/85	09:00	11:00	24.0	61.5	-0.13	23.3	249.5	234.0
5/22/85	13:00	15:00	24.0	61.5	-0.07	32.3	249.6	234.6
5/22/85	15:15	17:15	24.0	61.5	-0.10	35.1	352.5	324.0
5/22/85	18:00	20:00	23.5	61.0	0.12	32.4	468.5	422.0
5/24/85	06:00	08:00	23.5	61.0	-0.09	15.7	86.6	80.0
5/24/85	09:15	11:15	23.5	61.0	-0.09	23.1	122.0	113.6
5/24/85	12:00	14:00	23.5	61.0	-0.13	29.0	204.8	188.4
5/24/85	15:00	17:00	23.5	61.0	-0.26	32.8	276.0	252.5
5/24/85	18:00	20:00	23.5	61.0	-0.07	30.0	470.0	431.0

Figure 6. Air Concentration of Molinate

for 5/20/86 1800-2000
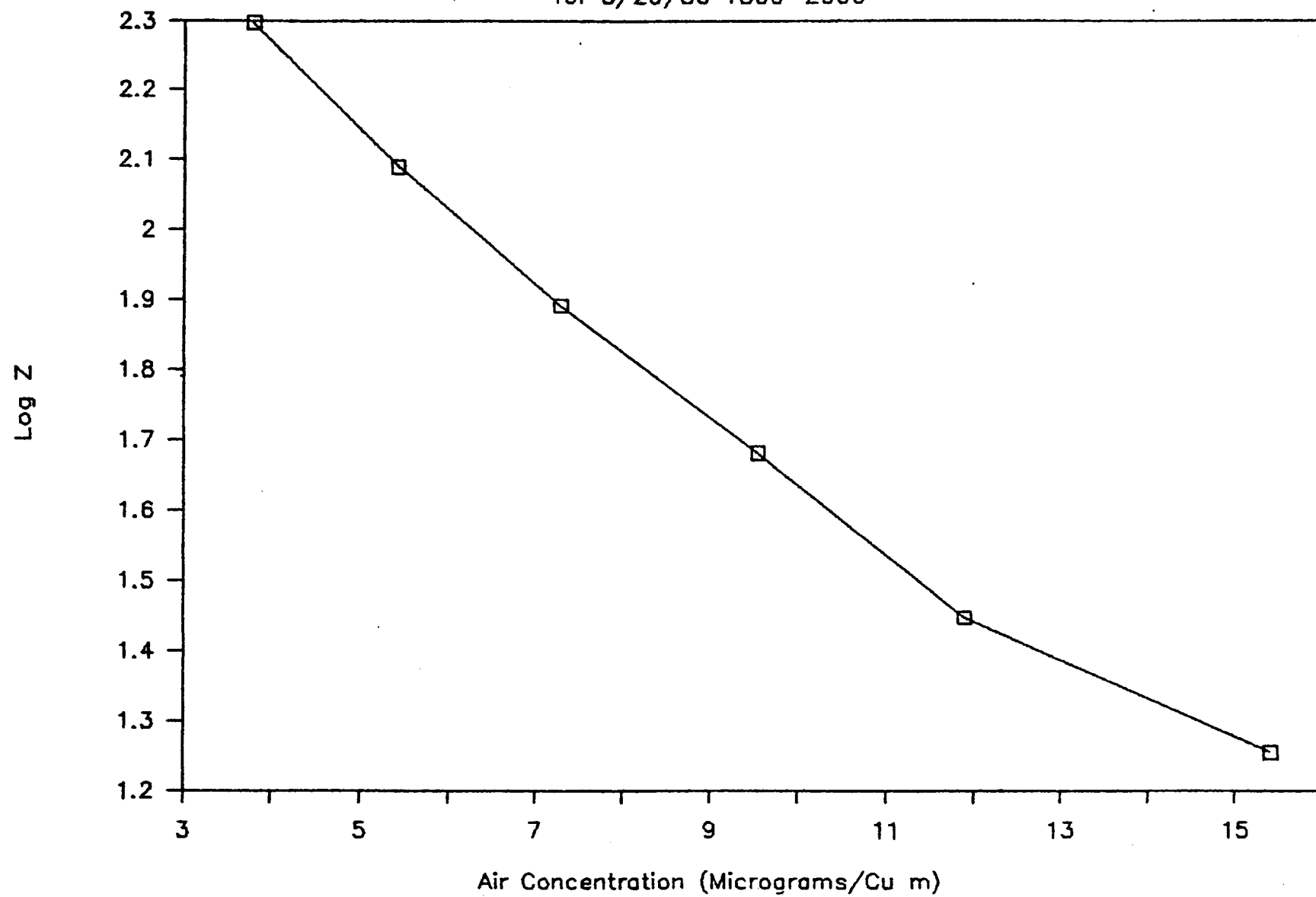
Table 13. Molinate Air Concentrations (µg/ Cu m.)
at Six Sampling Heights

DATE	TIME ON	TIME OFF	A	B	C	D	E	F
5/18/85	10:15	11:15	3.99	2.77	2.02	1.73	1.13	0.868
5/18/85	11:30	12:30	5.15	3.53	3.6		1.48	0.618
5/18/85	12:45	13:45	7.49	5.47	3.36	3.38	2.37	2.02
5/18/85	14:00	15:00	11	9.14	6.62	4.81	3.89	2.72
5/18/85	15:15	16:15	16.4	12.7	8.88	8.21	5.1	4.02
5/18/85	16:30	17:30	21.8	16.2	11	7.86	6.16	4.65
5/18/85	17:45	18:45	24.7	20.5	14.9	10.2	8.1	5.74
5/18/85	19:00	20:00	20.5	16.4	11.4	10.1	8.21	5.74
5/18/85	20:15	21:15	17.9	14.3	11.4	9.16	6.68	5.57
5/18/85	21:30	22:30	13.1	11.3	9.29	7.44	6.37	5.78
5/18/85	23:00	01:00	13	12.1	9.98	9.45	8.16	7.67
5/19/85	01:30	03:30	10.5	8.42	7.2	5.86	4.82	3.62
5/19/85	04:00	06:00	7.2	5.96	5.62	4.98	4.35	5.16
5/19/85	06:30	08:30	6.33	5.44	4.49	3.82	3.29	3.28
5/19/85	09:00	11:00	9.05	7.53	5.55	3.91	2.67	2.38
5/19/85	11:30	13:30	11.4	8.53	6.39	4.86	3.53	2.76
5/19/85	14:00	16:00	20.9	15.4	11.2	7.98	5.86	4.38
5/19/85	16:30	18:30	24.6	19.9	14.8	11.2	8.62	5.17
5/19/85	19:00	20:45	23.6	19	15.2	12.8	10.5	7.98
5/20/85	07:00	09:00	5.64	4.63	4.08	3.43	2.96	2.78
5/20/85	09:45	11:45	9.06	7.15	5.63	4.33	3.03	2.46
5/20/85	12:15	14:15	12.4	9.27	7.02	4.94	4.06	2.53
5/20/85	15:45	17:45	13.7	11	8.11	5.83	4.38	3.39
5/20/85	18:00	20:00	15.4	11.9	9.55	7.3	5.44	3.8
5/22/85	06:00	08:00	6.38	6.22	4.79	4.37	4.12	3.52
5/22/85	09:00	11:00	7.51	6.71	4.64	3.41	2.98	2.07
5/22/85	13:00	15:00	15.3	11.1	8.61	6.75	4.77	3.44
5/22/85	15:15	17:15	20.3	15.9	11.8	8.14	6.79	4.53
5/22/85	18:00	20:00	19.8	17.8	12.4	6.62	6.13	5.51
5/24/85	06:00	08:00	2.77	2.64	2.42	1.8	1.62	1.38
5/24/85	09:15	11:15	2.34	2.08	1.75	1.27	1.12	0.89
5/24/85	12:00	14:00	5	4.42	2.97	2.68	1.95	1.52
5/24/85	15:00	17:00	7.93	6.33	5.04	4.04	3.22	2.09
5/24/85	18:00	20:00	10.3	7.68	6.09	4.82	3.63	2.35

Table 14.   Molinate Air Concentrations at Two Heights Above
Field and Calculated Flux

DATE	TIME		Conc (μg/m^3) at heights		RICHARDSON NUMBER	DAVIS PROFILE	FLUX (ng/cm2/hr)
	ON	OFF	Z_2	Z_1			
5/18/85	10:15	11:15	1.94	2.86	-0.139	0.679	17.2
5/18/85	11:30	12:30	2.90	4.70	-0.202	0.621	29.2
5/18/85	12:45	13:45	3.85	5.75	-0.163	0.654	75.6
5/18/85	14:00	15:00	5.85	9.85	0.284	0.568	91.3
5/18/85	15:15	16:15	8.85	14.1	-0.235	0.598	116.0
5/18/85	16:30	17:30	9.10	18.6	-0.0465	0.832	92.5
5/18/85	17:45	18:45	11.7	16.5	-0.0280	0.885	126
5/18/85	19:00	20:00	12.0	17.5	-0.0106	0.950	105
5/18/85	20:15	21:15	10.4	15.3	-0.00646	0.968	46.2
5/18/85	21:30	22:30	8.4	12.13	-0.0349	0.864	47.2
5/18/85	23:00	01:00	10.0	12.8	-0.0770	0.767	44.7
5/19/85	01:30	03:30	6.55	9.00	-0.0482	0.828	21.4
5/19/85	04:00	06:00	5.28	6.62	-0.146	0.672	18.0
5/19/85	06:30	08:30	4.22	5.68	-0.170	0.648	58.1
5/19/85	09:00	11:00	4.85	7.90	-0.0494	0.825	25.7
5/19/85	11:30	13:30	5.70	7.50	-0.0681	0.784	138
5/19/85	14:00	16:00	9.70	17.0	-0.0798	0.762	154
5/19/85	16:30	18:30	14.0	21.50	-0.0186	0.918	84.6
5/19/85	19:00	20:45	14.4	19.9	-0.0167	0.925	12.8
5/20/85	07:00	09:00	3.75	4.89	-0.0860	0.752	71.2
5/20/85	09:45	11:45	5.00	8.30	-0.0204	0.911	53.7
5/20/85	12:15	14:15	6.10	10.1	-0.0514	0.820	84.0
5/20/85	15:45	17:45	7.00	12.3	-0.162	0.656	64.9
5/20/85	18:00	20:00	8.55	12.9	-0.0707	0.779	25.3
5/22/85	06:00	08:00	5.14	6.48	-0.0288	0.883	36.3
5/22/85	09:00	11:00	4.75	7.00	-0.0652	0.790	53.8
5/22/85	13:00	15:00	7.90	12.0	-0.0355	0.862	148
5/22/85	15:15	17:15	10.2	17.2	-0.0141	0.935	198
5/22/85	18:00	20:00	11.5	18.7	0.00687	1.04	8.25
5/24/85	06:00	08:00	2.14	2.82	-0.252	0.587	7.55
5/24/85	09:15	11:15	1.59	2.22	-0.152	0.666	25.8
5/24/85	12:00	14:00	3.11	4.73	-0.0572	0.807	45.3
5/24/85	15:00	17:00	4.75	6.75	-0.0558	0.810	69.0
5/24/85	18:00	20:00	5.60	8.25	-0.00529	0.974	0.145

Figure 7. Molinate Flux vs Time After Application.
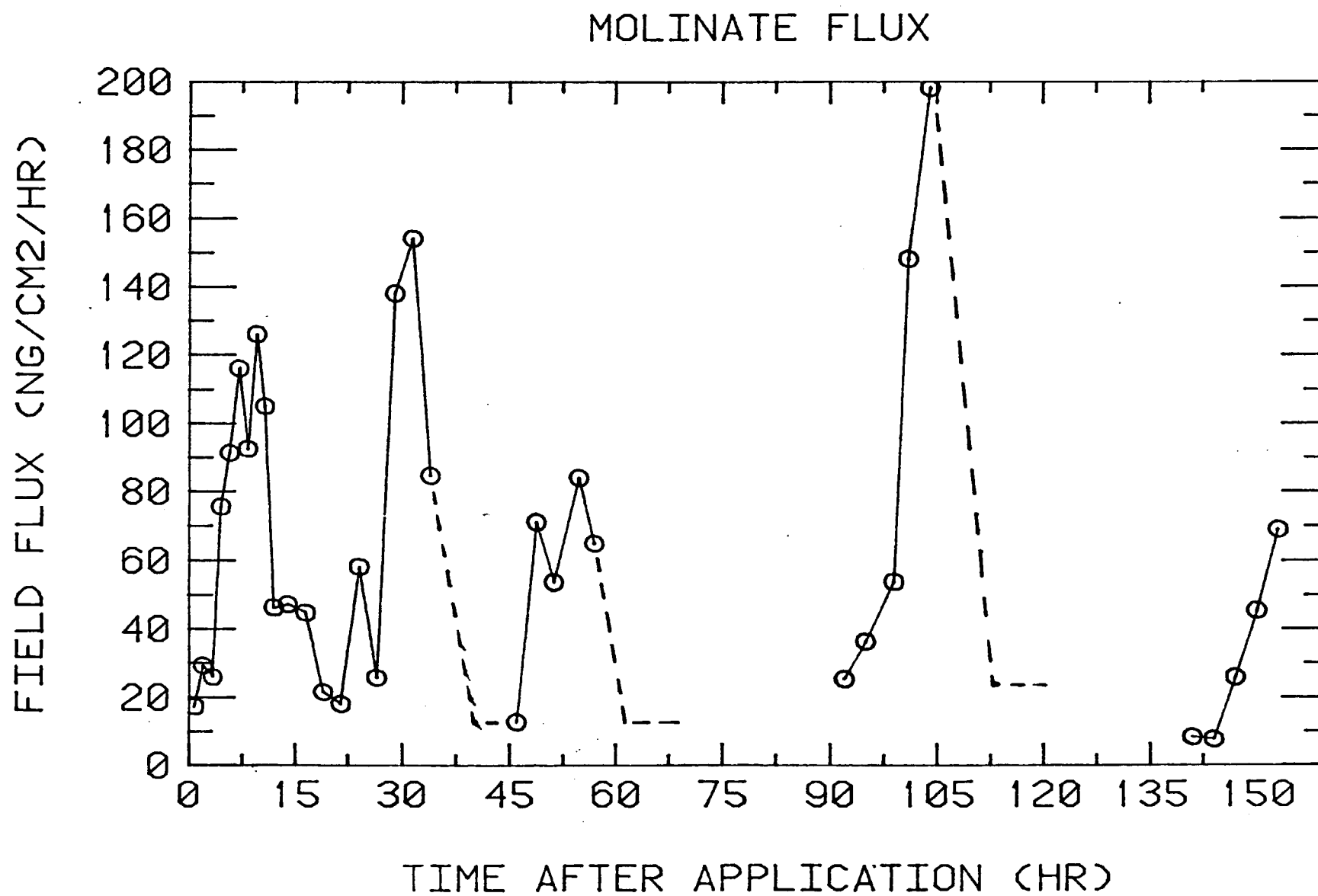
MOLINATE FLUX

Corresponding flux values for methyl parathion are in Table 15 and 16 and
Figure 8. The flux values for methyl parathion were considerably lower (about
1/100th) than those for molinate. The profiles were somewhat more eratic,
perhaps reflecting a larger analytical error due to the smaller concentra-
tions, and did not show as clear a trend toward maximum flux values at early
evening. Minima did occur in early morning, as for molinate. The maximum
flux values for methyl parathion ranged from 0.23 (day 3) to 0.82 ng/cm^2/hr
(days 1 and 2).

In the 1983 flux study of molinate flux, we established that 1.1 kg/ha
was lost by volatilization during the first 4 days intervening after
application of molinate. The calculation involved obtaining the average
volatilization rate (ng/cm^2/hr) for the daylight hours of each day, then
multiplying by 12 hr and the conversion factor (9.86×10^{-5}) for converting
ng/cm^2 to kg/ha. Corresponding data for the two years are thus:

| | 1983 Flux | | 1985 Flux | |
Day	ng/cm^2/hr	kg/ha	ng/cm^2/hr	kg/ha
0	575	0.68	72.5	0.086
1	193	0.22	79.7	0.094
2	110	0.13	57.3	0.067
3	58	0.07		———
			Total =	0.247
		———		
	Total =	1.1		

Table 15. Methyl Parathion Air Concentrations (ng/m³) at Six Heights

DATE	ON	OFF	A	B	C	D	E	F
5/18/85	10:15	11:15	36.1	29.0	25.3	24.4	17.7	16.2
5/18/85	11:30	12:30	45.1	39.0	28.9	24.8	18.3	12.0
5/18/85	12:45	13:45						
5/18/85	14:00	15:00	61.3	57.5	38.8	32.0	18.8	34.7
5/18/85	15:15	16:15	54.3	49.4	27.3	33.0	37.1	13.6
5/18/85	16:30	17:30	103		65.3	39.4	53.4	28.9
5/18/85	17:45	18:45	129	94.1	82.5	51.5	45.2	28.5
5/18/85	19:00	20:00	35.8	92.4	97.7	57.0	43.0	19.4
5/18/85	20:15	21:15	129	87.0	81.3	72.3	64.1	51.8
5/18/85	21:30	22:30	78.5	60.1	59.3	84.5	36.0	44.4
5/18/85	23:00	01:00	136	114	103	64.7	62.1	85.2
5/19/85	01:30	03:30	152	77.8	60.1	20.2	46.8	29.5
5/19/85	04:00	06:00	49.1	35.8	39.7	34.8	31.7	35.6
5/19/85	06:30	08:30	64.6	56.6	51.4	36.1	34.3	30.6
5/19/85	09:00	11:00	40.6	38	36.9	32.3	30.4	26.8
5/19/85	11:30	13:30	41.9	30.5	28.5	19.5	23.2	13.9
5/19/85	14:00	16:00	47.1	51.8	34.2	23.7	19.5	17.3
5/19/85	16:30	18:30	94.0	67.5	60.3	36.7	30.5	31.5
5/19/85	19:00	20:45	132	107	62.6	45.3	73.6	
5/20/85	07:00	09:00	15.5	18.2	12.7	12	12.3	12.4
5/20/85	09:45	11:45	25.8	15.1	14.7	15.4	11.4	4.56
5/20/85	12:15	14:15	31.1	24.5	15.8	29.0	11.9	10.4
5/20/85	15:45	17:45	25.5	19.7	16.2	4.54		7.99
5/20/85	18:00	20:00	42.2	46.3	22.4	34.3	13.2	27.7
5/22/85	06:00	08:00	307	290	202	60.6	204	33
5/22/85	09:00	11:00	152	222	186	146	169	162
5/22/85	13:00	15:00	196	193	150	158	158	154
5/22/85	15:15	17:15	101	38.5	212	171	219	158
5/22/85	18:00	20:00	149	198	240	376	150	175
5/24/85	06:00	08:00	46.9	26.7	28.5	26.8	17.1	14.
5/24/85	09:15	11:15	4.81	6.12	4.64	3.89	2.6	2.93
5/24/85	12:00	14:00	10.6	8.73	5.73	4.82	4.64	10.7
5/24/85	15:00	17:00	21.2	11.4	9.45	4.64		11.4
5/24/85	18:00	20:00	26.9	29.6	25.7	23.7	20.8	15.2

Table 16.   Methyl Parathion Air Concentrations at Two Heights Above
Field and Calculated Flux

	DATE ON	TIME OFF	Conc (ng/m^3) at heights Z_2	Z_1	RICHARDSON NUMBER	DAVIS PROFILE	FLUX (ng/cm2/hr)
5/18/85	10:15	11:15	24.3	31.2	-0.139	0.679	0.129
5/18/85	11:30	12:30	26.8	39.0	-0.202	0.621	0.197
5/18/85	12:45	13:45	0.0	0.0	-0.163	0.654	0.0
5/18/85	14:00	15:00	34.3	53.5	0.284	0.568	0.362
5/18/85	15:15	16:15	35.9	53.0	-0.235	0.598	0.297
5/18/85	16:30	17:30	58.0	89.0	-0.0465	0.832	0.378
5/18/85	17:45	18:45	72.0	111.	-0.0280	0.885	0.749
5/18/85	19:00	20:00	66.0	98.0	-0.0106	0.950	0.732
5/18/85	20:15	21:15	75.0	98.0	-0.00646	0.968	0.492
5/18/85	21:30	22:30	52.0	73.3	-0.0349	0.864	0.265
5/18/85	23:00	01:00	76.0	124.	-0.0770	0.767	0.823
5/19/85	01:30	03:30	53.0	83.0	-0.0482	0.828	0.546
5/19/85	04:00	06:00	36.7	44.0	-0.146	0.672	0.116
5/19/85	06:30	08:30	44.8	60.0	-0.170	0.648	0.187
5/19/85	09:00	11:00	33.6	39.1	-0.0494	0.825	0.105
5/19/85	11:30	13:30	30.0	40.5	-0.0681	0.784	0.15
5/19/85	14:00	16:00	28.6	58.0	-0.0798	0.762	0.555
5/19/85	16:30	18:30	47.5	85.0	-0.0186	0.918	0.767
5/19/85	19:00	20:45	69.0	122.	-0.0167	0.925	0.814
5/20/85	07:00	09:00	0.0	0.0	-0.0860	0.752	0.0
5/20/85	09:45	11:45	17.4	25.2	-0.0204	0.911	0.168
5/20/85	12:15	14:15	12.9	29.1	-0.0514	0.820	0.217
5/20/85	15:45	17:45	15.7	21.9	-0.162	0.656	0.098
5/20/85	18:00	20:00	31.6	44.0	-0.0707	0.779	0.184
5/22/85	06:00	08:00	0.0	0.0	-0.0288	0.883	0.0
5/22/85	09:00	11:00	0.0	0.0	-0.0652	0.790	0.0
5/22/85	13:00	15:00	0.0	0.0	-0.0355	0.862	0.0
5/22/85	15:15	17:15	0.0	0.0	-0.0141	0.935	0.0
5/22/85	18:00	20:00	0.0	0.0	0.00687	1.04	0.0
5/24/85	06:00	08:00	3.10	4.40	-0.252	0.587	0.016
5/24/85	09:15	11:15	4.4	6.6	-0.152	0.666	0.026
5/24/85	12:00	14:00	5.9	9.9	-0.0572	0.807	0.064
5/24/85	15:00	17:00	7.9	18.5	-0.0558	0.810	0.24
5/24/85	18:00	20:00	25.2	30.8	-0.00529	0.974	0.145

Figure 8. Methyl Parathion Flux <u>vs</u> Time.

METHYL PARATHION FLUX
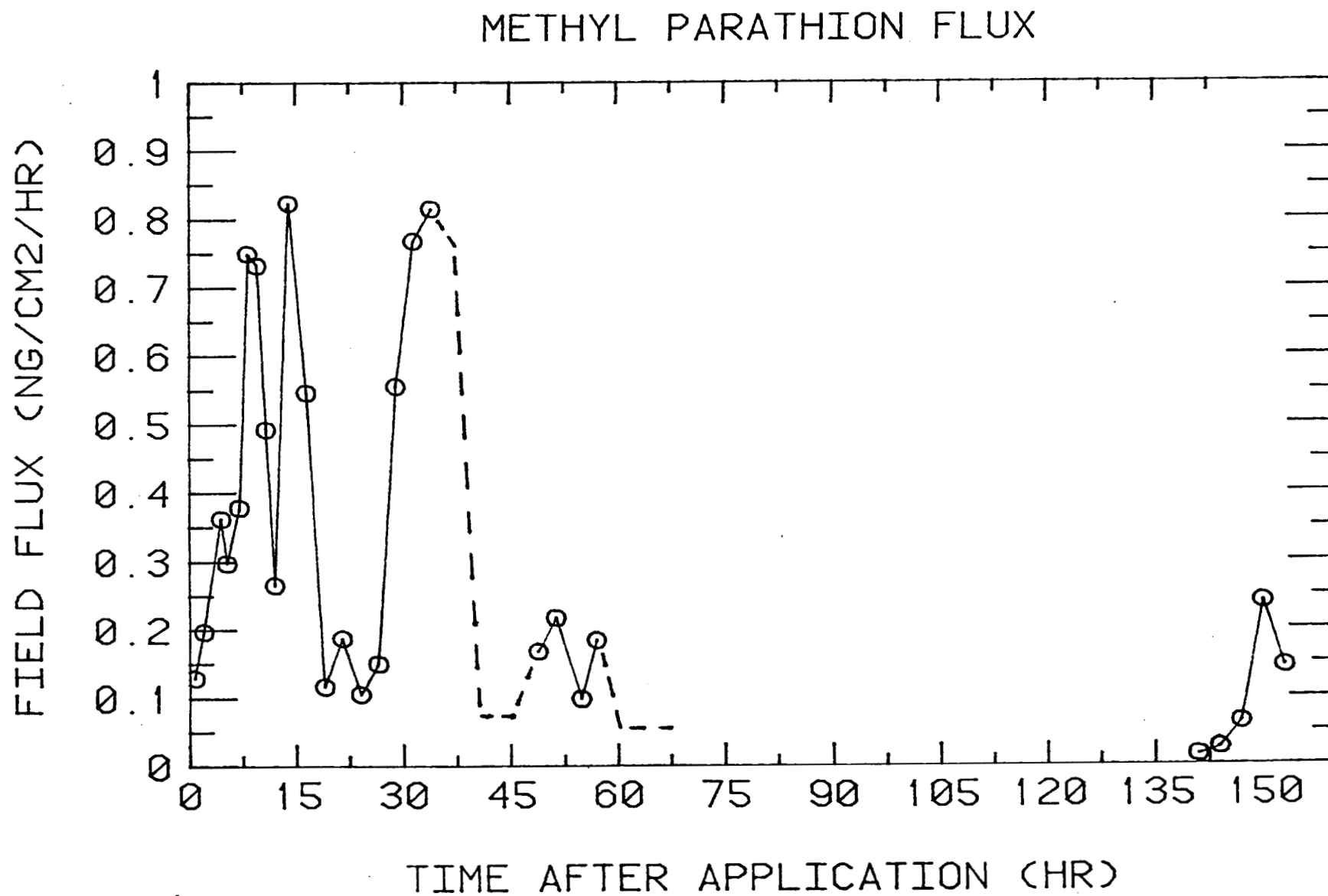
On this basis, the 1983 flux was considerably higher than for 1985. However, the 1983 field received a double application of molinate (the 1st preceding the 2nd, monitored, application by 5 days) and thus had a higher water concentration (by about 50%) throughout the days flux measurements were made. Second, the high day 0 flux value for 1983 may have been an anomaly. Thus, a better comparison might be for days 1-3 of 1983 with days 0-2 of 1985. When that comparison is carried out, and account is made of the higher water concentration in 1983, the measured flux is more comparable for the two years although still somewhat higher for the 1983 samplings.

If one assumes that the average volatilization rate of molinate is 0.082 kg/ha/12 hrs (0.247 ÷ 3), 0.58 kg would be lost in 7 days by volatilization during daylight hours. If 3.94 kg/ha were applied (Application rate of 4.48 kg/ha x application efficiency of 88%), this corresponds to 13% lost by volatilization in that time period. Obviously, this is only a very approximate figure primarily because of the large error introduced in using average volatilization figures to represent all daylight hours. Rates could have been substantially different from the average for any given interval, including the many intervals when no sampling was conducted. However if volatilization is the major pathway of loss, the flux rate determined is considerably lower than expected considering the change in molinate concentration in water during the test interval.

In order to obtain more information on the relative importance of volatilization vs other fate processes (hydrolysis, microbial breakdown, irreversible adsorption), molinate was dissolved in water and added to two sets of Mason jars containing water and sediment in the same ratio occurring in the field. The jars were then partially submerged in the field to maintain identical temperature, sunlight, etc as occurred in the field. The water

concentration of molinate was then determined at various intervals in a set of
jars which were kept sealed (no volatilization) and in the second set which
were left open (volatilization possible). The results (Table 17, Figure 9)
showed a rate of loss in the open jars ($t\frac{1}{2} \cong 70$ hr) nearly identical to that
in the rice field, but a substantially slower loss ($t\frac{1}{2} > 220$ hr) when the
jars were sealed. This confirms that volatilization is the major loss of
molinate under these conditions, and infers that the volatilization loss
approximated from the aerodynamic flux measurements is lower than what
actually occurred.

Exposure Analysis Modeling System (EXAMS)

The second objective of the project was to compare the vertical field
flux to a predicted flux from a computer model. Exposure Analysis Modeling
System (EXAMS) is a sophisticated FORTRAN program developed for the United
States Environmental Protection Agency to model the fate of pollutants in
aquatic ecosystems. A PDP-11 version of the program was installed on the UCD
VAX 11/750 computer with a VMS operating system. However, the program had to
be modified before it could be successfully used. Several weeks of
verification followed before rice field parameters could be entered into the
system.

EXAMS uses differential equations to calculate the amount of chemical
lost from water by volatilization, hydrolysis, microbial breakdown, and the
like. Variables include the physico-chemical properties of the chemical,
properties of the environment modelled (pH, wind speed, temp, microbial
activity, etc), and parameters describing the size of the water, soil, air,
and biotic compartments in the environment studied. We hypothesized that, by
setting up EXAMS with the properties of molinate or methyl parathion along

Table 17. Rate of Dissipation of Dissolved Molinate From Jars Partially

Submerged in a Rice Field.

| | Water Concentration, ppm | |
Time	Open Jars	Closed Jars
0 hr	1.30	1.51
3.5 hr	1.50	--
6.5 hr	1.33	1.33
39.5 hr	1.10	1.49
53	0.92	--
73	0.70	1.19
222	0.27	1.14

Figure 9. Dissipation of dissolved molinate from the water of jars kept partly submerged in a rice field. Circles denote closed jars, stars denote open jars.
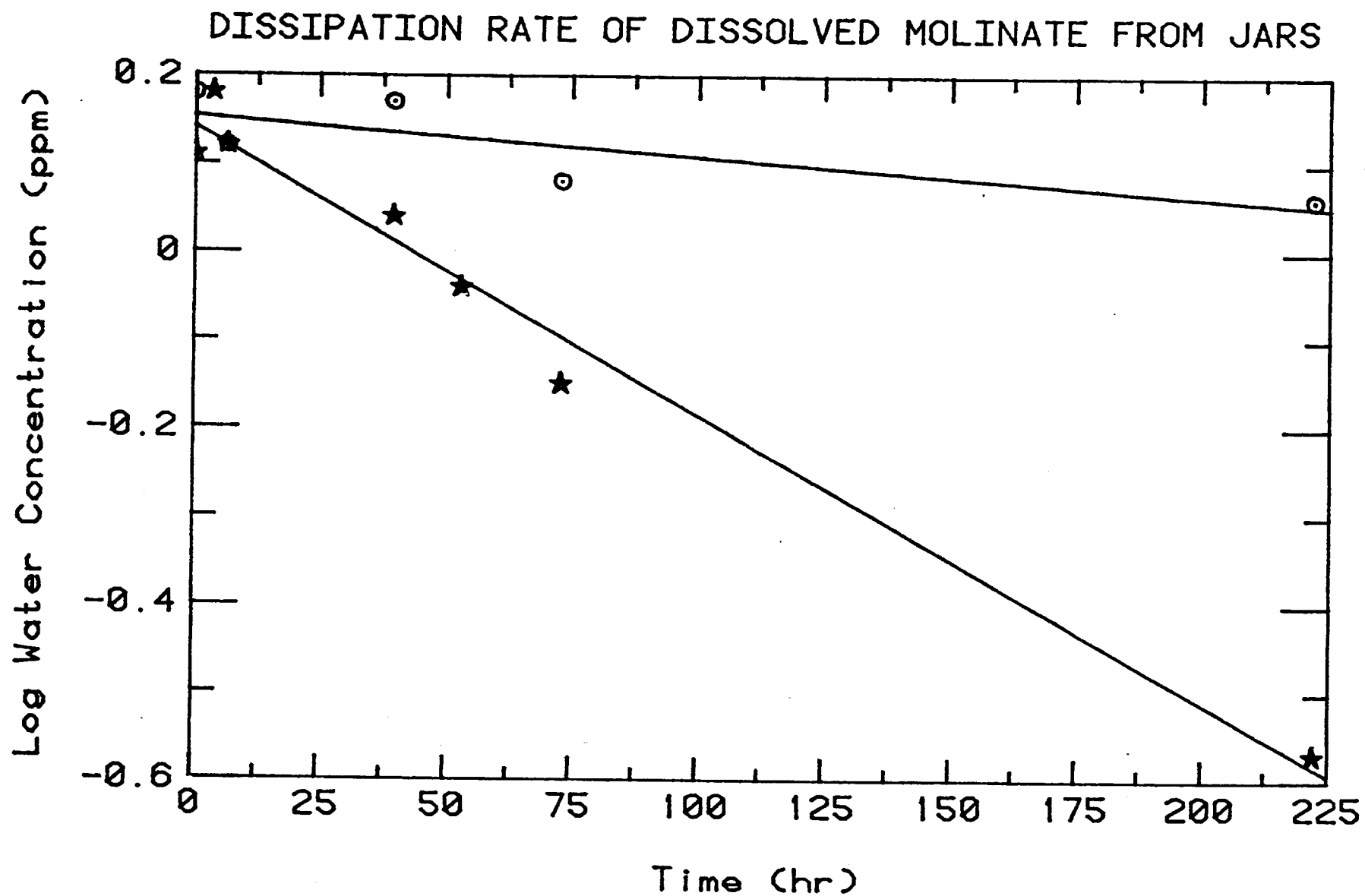
with the weather conditions and dimensions of the rice field, EXAMS could calculate the rate of a given fate process (volatilization in this case) which could then be compared with observed rates. If the comparison was favorable, EXAMS could then be considered validated and then used to predict rates for other chemicals and environmental conditions.

In choosing variables for correlating with volatilization, we first looked qualitatively at the four environmental parameters which we assumed might have a direct bearing on it. These were water depth (Figure 10), pH (Figure 11), temperature (Figure 12) and windspeed (Figure 13) -- the latter expected to have an indirect effect on flux because a competing process (hydrolysis) is pH dependent. Of the three, both temperature (Figure 12) and wind speed (Figure 13) showed a qualitative correlation, with periods of high temperature and high wind speed corresponding roughly with periods of maximum flux (CF Figures 7 and 8). Water depth did not change significantly with time during the study period (Figure 10), nor did pH (Figure 11).

EXAMS can be used to calculate volatilization flux by entering or changing the following data:

1. The wind speed at 10 cm (WINDG(1)) must be calculated using the log law:

$$U_2 \text{ LOG } (Z_1/Z_0)/(Z_2/Z_0) = U_1$$

where Z_0 is the roughness height (1 mm for water).

WINDG(1) is the wind speed in m/sec. $= U_1$

2. The oxygen exchange rate KO2G(1) (aeration rate) must be determined by computing the wind speed at 10 meters, then using the following equation:

Figure 10. Average Water Depth in Paddy vs Time After Application.

WATER DEPTH (CM) VERSUS TIME (HRS)

DEPTH (CM)

TIME AFTER APPLICATION (HRS)
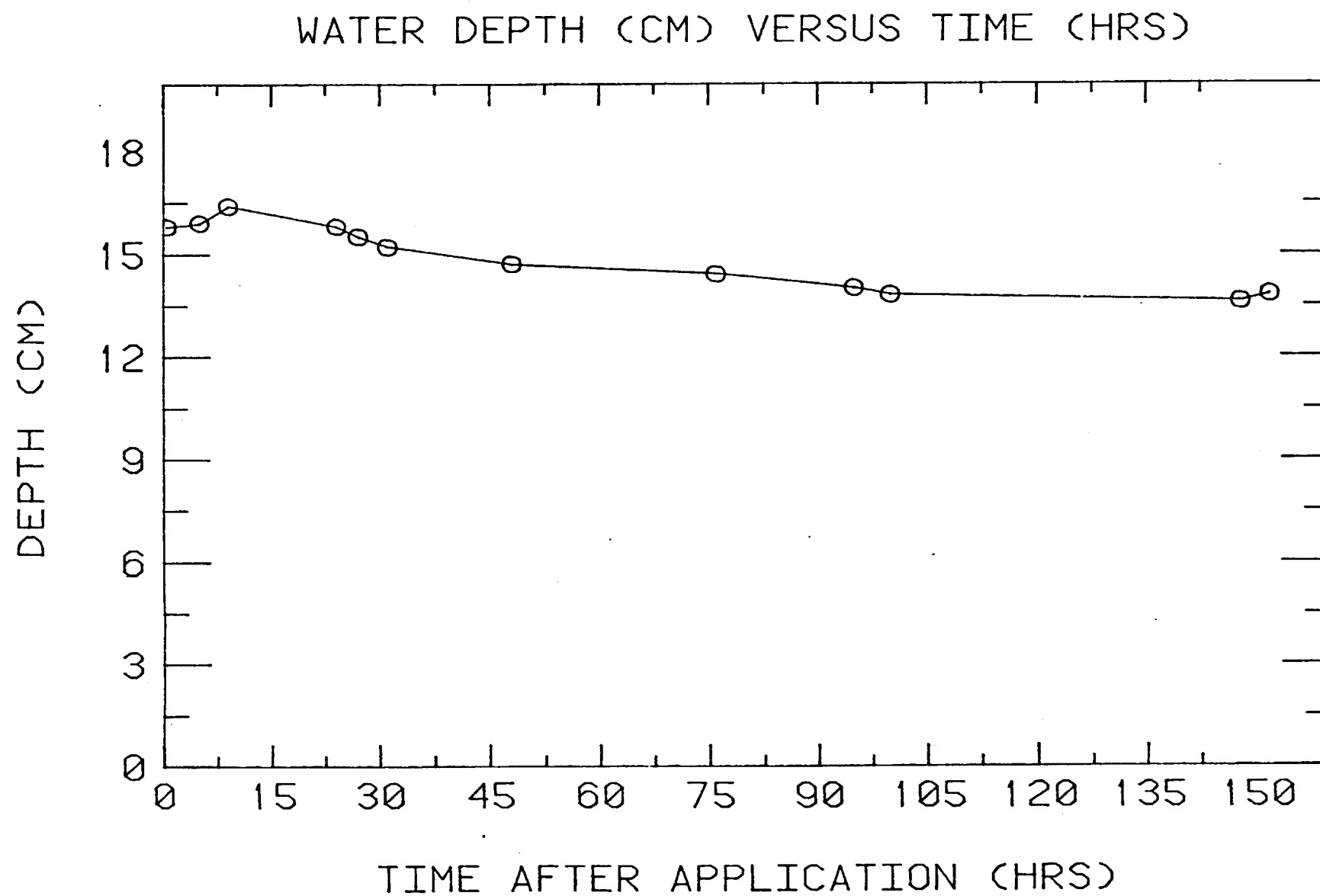
Figure 11. Water pH vs Time After Application in Paddy.

PH VERSUS TIME FOR RICE FIELD
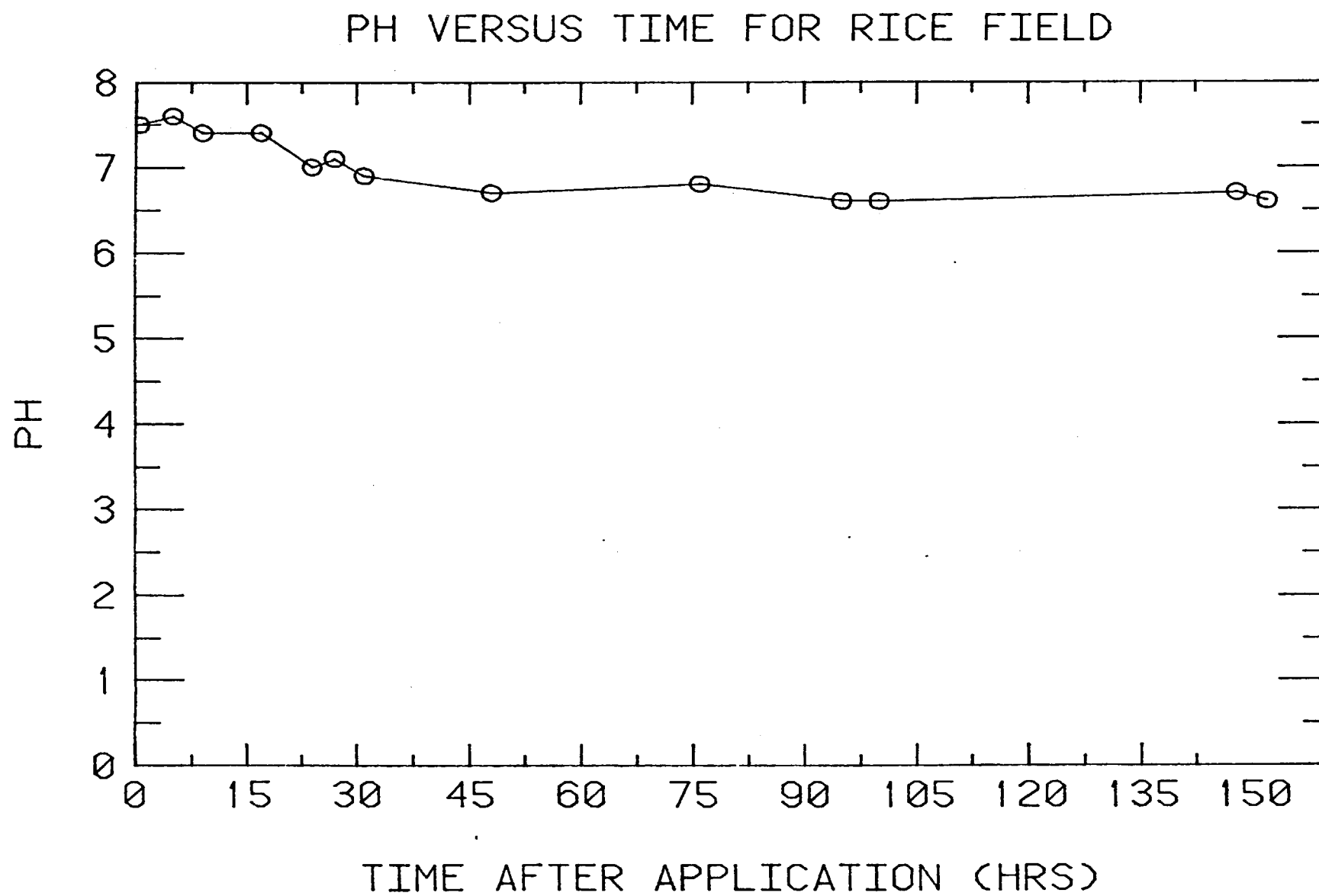
Figure 12. Water Temperature <u>vs</u> Time After Application in Paddy.

WATER TEMPERATURE VERSUS TIME AFTER APPLICATION
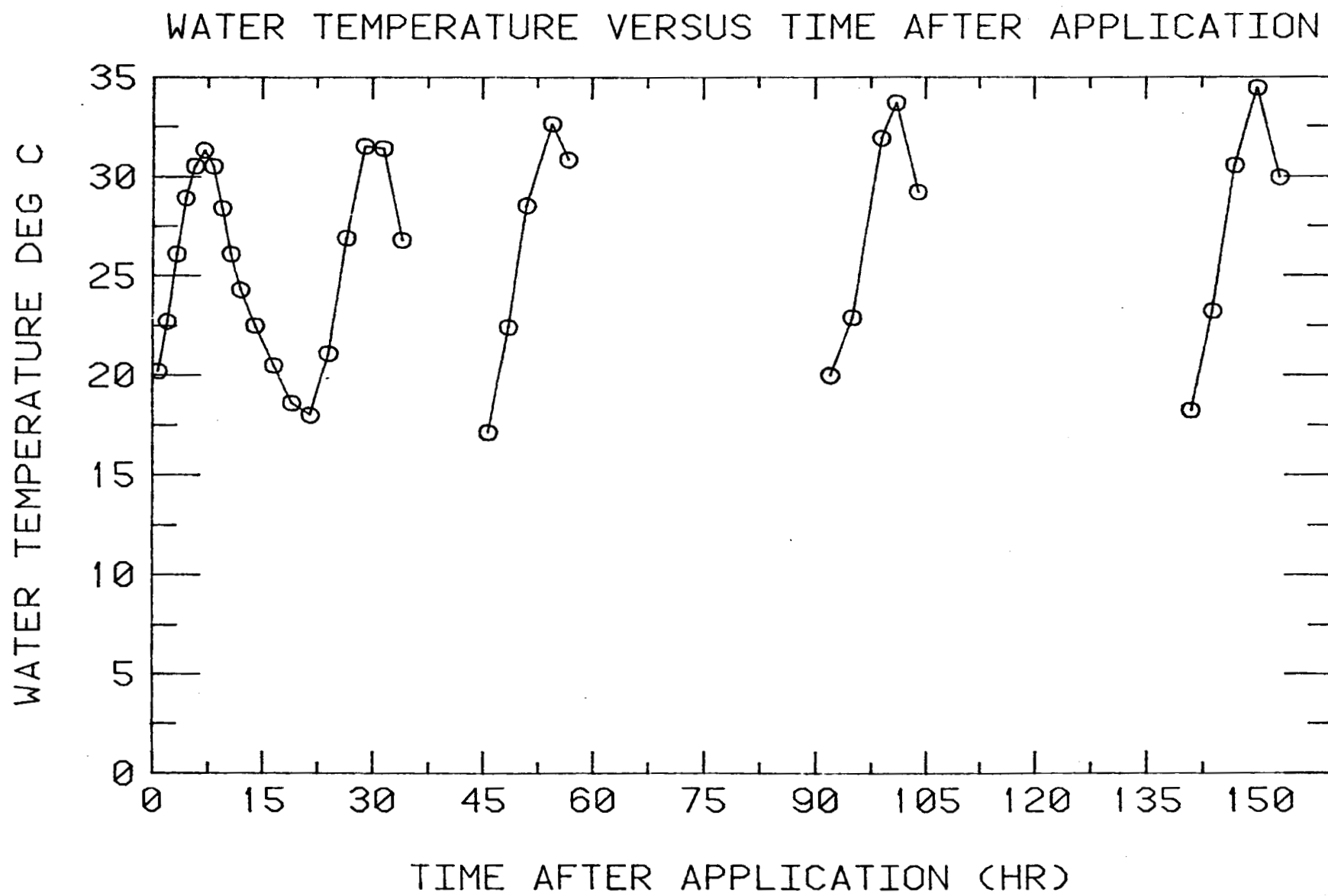
Figure 13. Windspeed Above Paddy <u>vs</u> Time After Application.

WIND SPEED CM/MIN VERSUS TIME AFTER APPLICATION

50
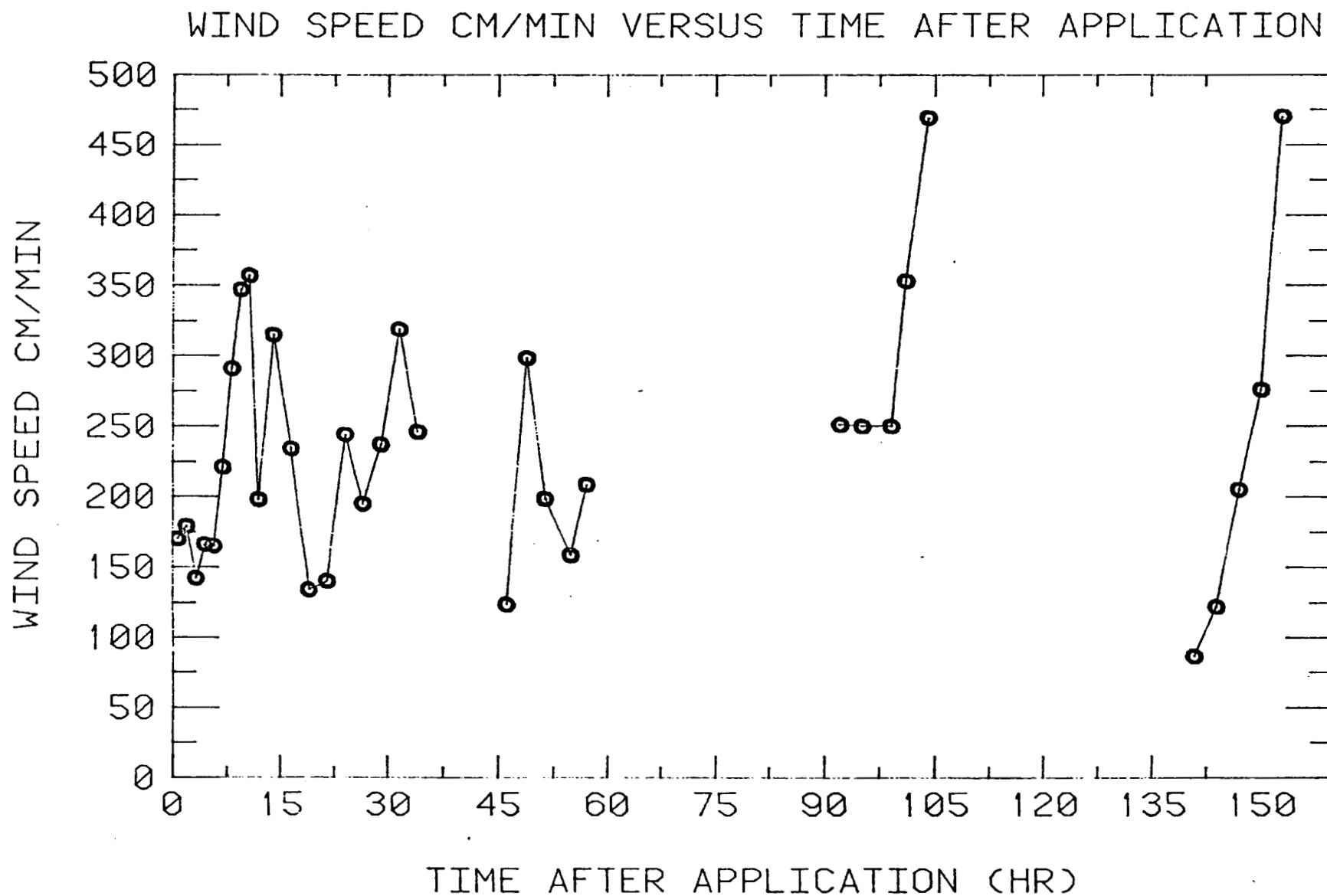
$$KO2G(1) = 3.6E5*KL$$

$$KL = (4.96E-6)SQRT(U) \qquad \text{(for U < 5.5 m/sec)}$$

$$KL = (3.2E-7)*U^2 \qquad \text{(for U > 5.5 m/sec)}$$

where U is the wind speed in m/sec.

3.   The solubility [sol (1)] and the vapor pressure (VAPR) must be calculated for each temperature.

The vapor pressure for methyl parathion was calculated from the equation (Kim et al., 1984):

$$\log P = 17.0502 - 6520.23/T$$

The solubility of methyl parathion was estimated using the rule of the thumb that the solubility increases by a factor of 2 for every 14 degrees rise in temperature. Because the log P _vs_ T relationship for molinate was not known, nor was the effect of T on solubility, estimates were made as noted below.

Once vapor pressure and solubility had been determined for each sampling period, an environment was selected from the EXAMS data base or the user data base. For example, for molinate the environment used was a laboratory chamber (water with negligible sediment). In order to adapt the lab chamber model to the commercial field situation the following changes were made:

1. changed area of compartment 1 [area(1)] to 95506 m^2

2. changed volume of compartment 1 [vol(1)] to 16235 cu m^3

3. changed depth of compartment 1 [depth(1)] to 0.17 m

4. changed volume of compartment 2 [vol(2)] to 95506E-4 m^3

5. changed area of compartment 2 [area(2)] to 95506 m^2

     where compartment 1 is the littonal and compartment 2 is the benthic compartment.

It should be noted that no fate process other than volatilization can take place with this particular environment. After making changes for the environment and recalling a chemical, a load must be specified and, in this case, a drift load [drfld(1)] of 1.0 E-2 Kg/hr was given.

Normalized flux from EXAMS data was calculated using the volitilization rate constant from Table 10 of the EXAMS output. The rate constant has units of 1/hr and can be expressed as follows:

$$1/hr = 1/hr \times \frac{P.P.M.}{P.P.M.} = 1/hr \times \frac{\mu g/gr}{P.P.M.} = 1/hr \times \frac{\mu g/cm^3}{P.P.M.}$$

The units of normalized field flux are: $\quad 1/hr \times \dfrac{ng/cm^2}{P.P.M.}$

therefore, normalized flux for EXAMS = rate constant x 1000 x water depth in cm.

A major obstacle was encountered in using EXAMS for molinate flux; the effect of temperature on molinate's vapor pressure or water solubility was not recorded in the literature and thus was approximated. For P vs T, we used the known relationship for another thiolcarbamate, EPTC, and adjusted the literature vapor pressure of molinate (3.71×10^{-3} Torr at 20°C) accordingly. For water solubility vs temperature we looked at reported (Freed et al., 1967) data for 4 carbamates (CIPC, IPC, Barban, and BCPC) which show a "regular" dependence, ie solubility increases with increasing temperature, and also for one thiolcarbamate (EPTC) which shows an "inverse" dependence (Table 18). The latter was chosen for adjusting the literature solubility for molinate (800 ppm at 20°C) because of the structural similarity of molinate and EPTC.

It is reported (Rummens and Louman, 1970) that EPTC and other thiolcarbamates show "inverse" behaviour because the less polar N-C = O is

Table 18. Estimated Effect of Temperature on Vapor Pressure
and Water Solubility of Molinate.

Temp	Vapor Pressure[a]	Water Solubility	
		Regular[b]	Inverse[c]
15°C	2.45×10^{-3} Torr	600	912
20	3.71	800	800
25	5.60	1000	688
28	7.00	1150	621
30	8.16	1200	576
35	11.74	1400	464

[a] Based on EPTC, that is, the literature vapor pressure of molinate was corrected by the EPTC vapor pressure-temperature dependence.

[b] Based on average from 4 carbamates

[c] Based on EPTC

favored over the more polar $\overset{+}{N} = C - \overset{-}{O}$ resonance structure as temperature is increased. The temperature dependence of S is critically important to flux because Henry's law constant -- a prime determinant of flux from water -- has a direct dependence on the ration of P to S. The effect can be seen in Figure 14 for molinate assuming that it had "regular" dependence of S or T; because both P and S increase with increasing temperature in this assumption, the effects largely cancel and flux shows only a minor temperature dependence. Figure 15 shows the same plot for molinate assuming an "inverse" dependence of S on T, with flux greatly increasing with increasing T. These EXAM simulation runs were done for molinate volatilizing from a dish of water, although the effect should be the same for water in a rice field.

Another EXAMS simulation was run in which the wind speed was changed to see what effect that would have on the volatilization flux. A wind speed of zero could not be entered or the simulation would take more computation time than allowed by EXAMS.

Figure 16 shows that the resulting flux vs wind speed is linearly correlated.

The appropriate field-measured wind speed, water temperature, vapor pressure, and water solubility for each flux sampling period was then used as input for EXAMS, and the computer model calculated the volatilization rate constants for molinate (Table 19). The rate constants were then converted to flux (normalized on water concentration) for comparison with field-measured flux (also normalized on water concentration) (Table 20). A graphical comparison of the two (Figure 17) showed that EXAMS correctly predicted the overall shape of the flux vs time profile, catching both the maxima and minima. EXAMS, however, gave values roughly 2 x those measured in the field for 4 of the 5 maxima for which data was available. This confirms the general
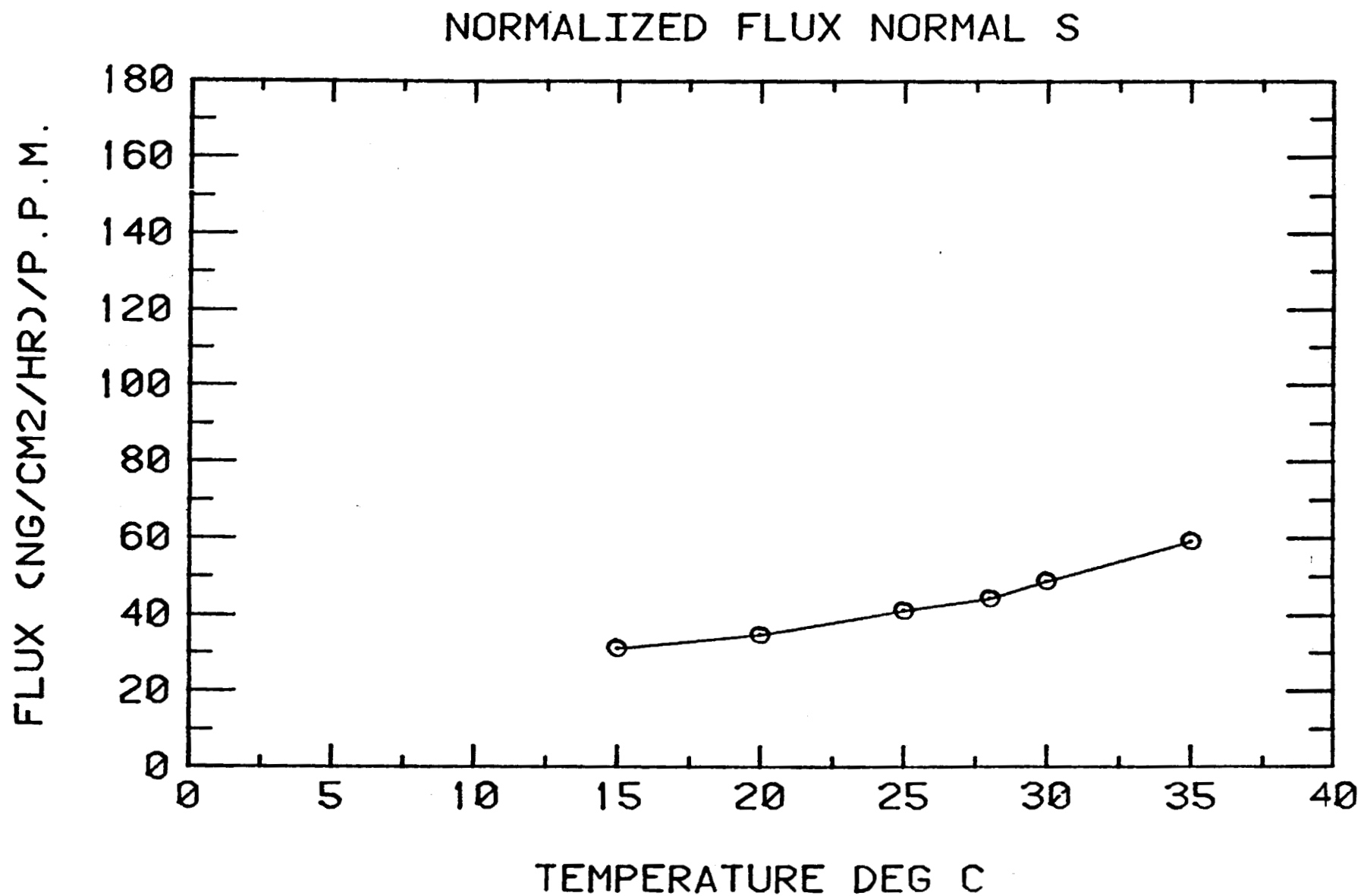
NORMALIZED FLUX NORMAL S

Figure 15. EXAMS-calculated Flux as a Function of Temperature for Molinate
Assuming an Inverse Dependence of Solubility on Temperature.

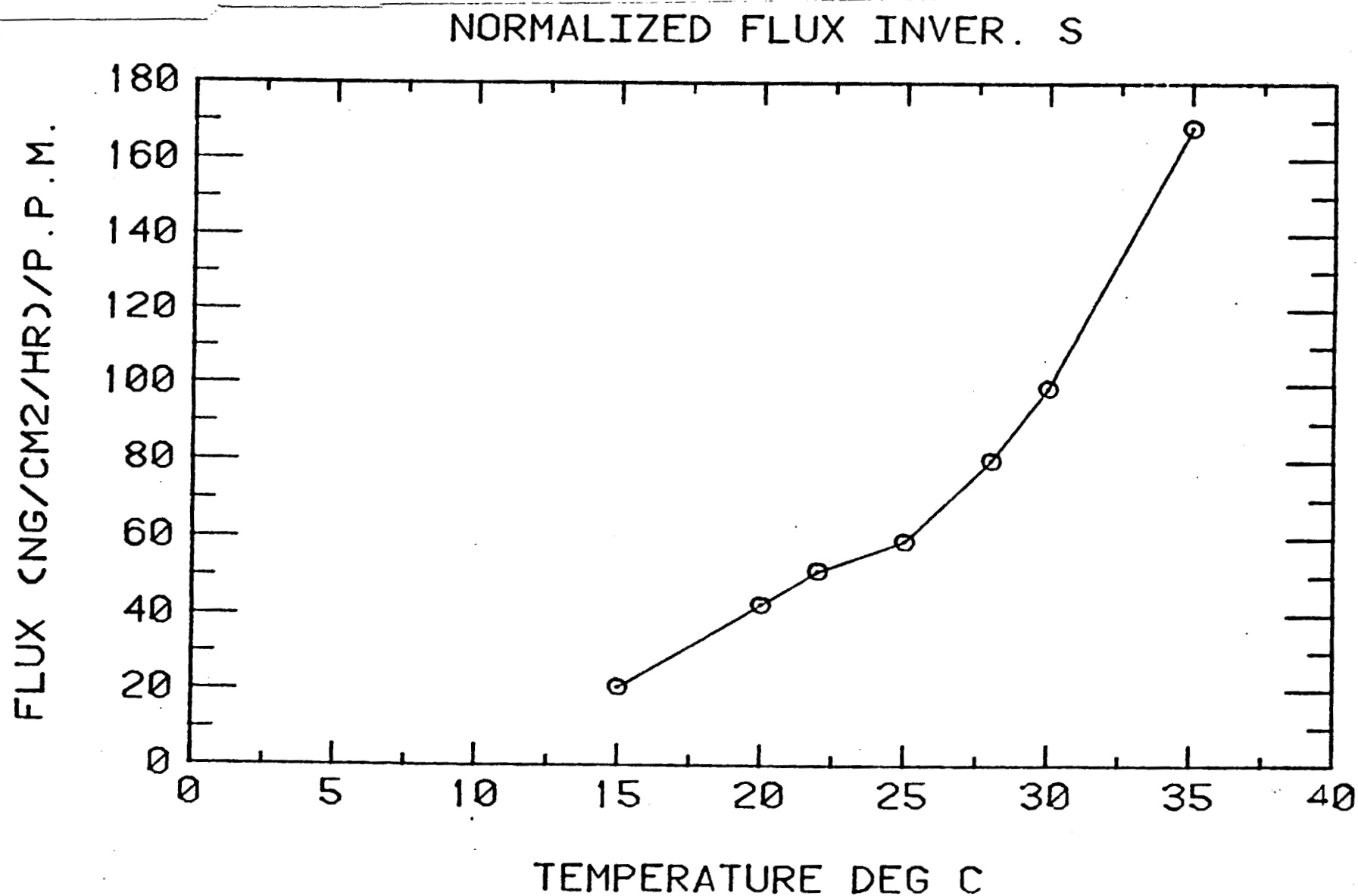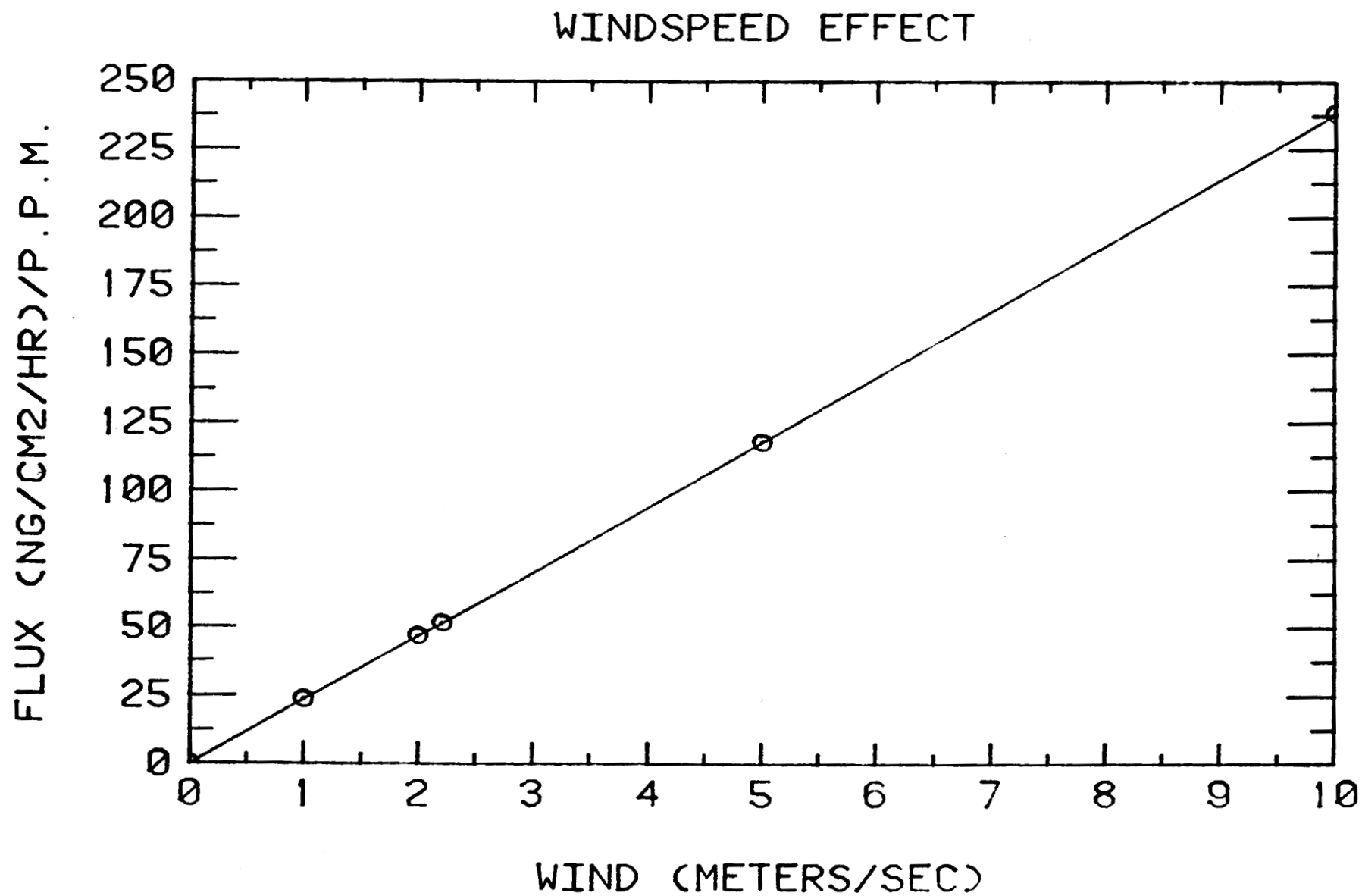NORMALIZED FLUX INVER. S

WINDSPEED EFFECT

57

Table 19. Data for EXAMS Calculation of Volatilization Rate Constant

EXAMS DATA FOR MOLINATE

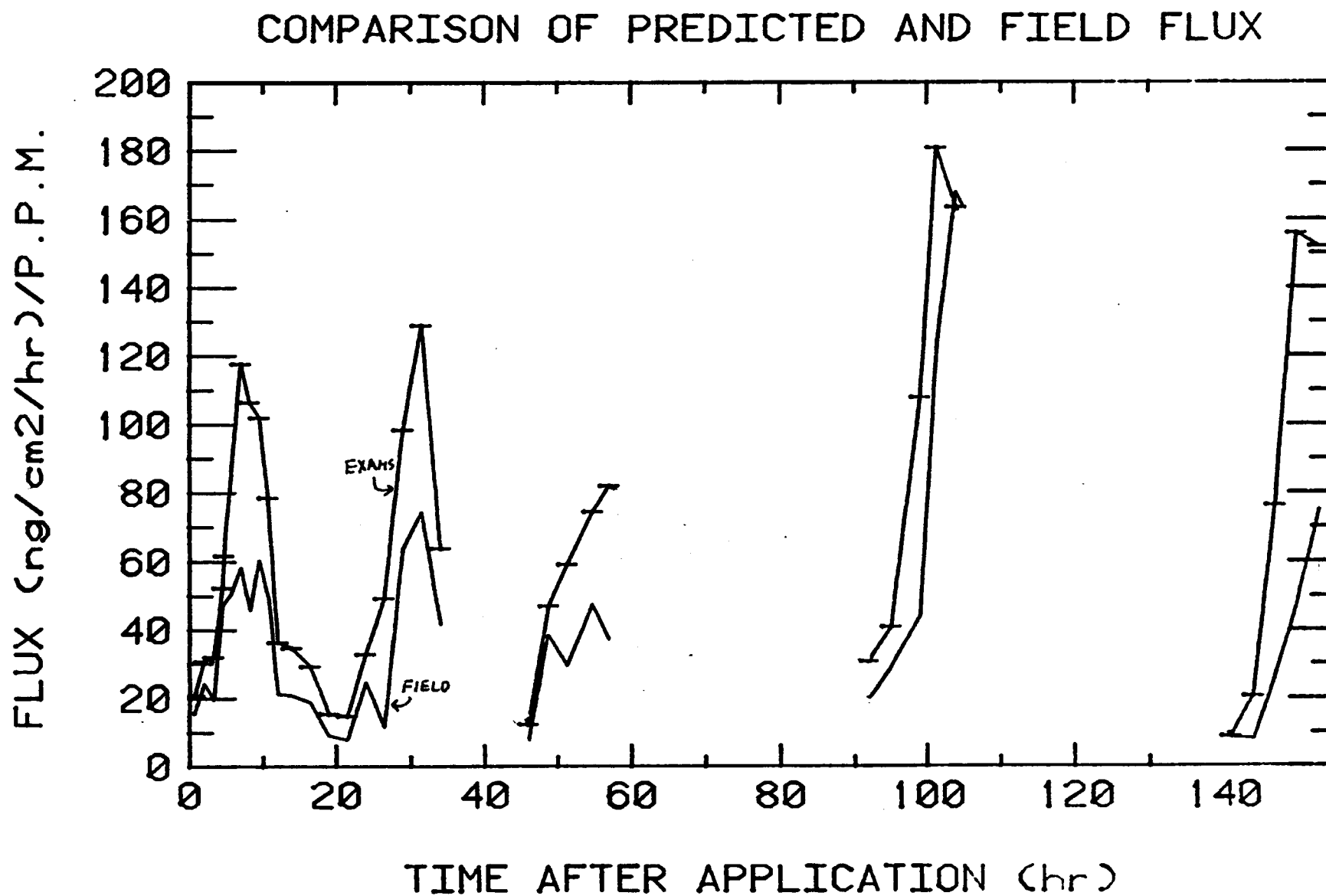| TIME	WIND (m/sec)	KO2G(1)	TCEL (C)	VAPR[a] (E-3)	SOL(1) (PPM)	RATE,K (E-3/hr.)
0.75	1.33	2.47	20.2	3.71	800	5.034
2.0	1.39	2.52	22.7	4.55	690	7.357
3.3	1.11	2.25	26.1	5.85	670	7.695
4.5	1.29	2.43	28.9	7.53	600	1.249
5.75	1.29	2.42	30.5	8.50	570	1.473
7	1.72	2.80	31.3	9.0	560	2.82
8.25	2.27	3.22	30.5	8.50	570	2.538
9.5	2.70	3.51	28.4	7.25	610	2.432
10.7	2.78	3.57	26.1	5.85	670	1.877
12.0	1.54	2.65	24.3	5.10	715	8.737
14.0	1.60	2.70	22.5	4.50	695	8.29
16.5	1.82	2.88	20.5	3.75	790	6.993
19.0	1.05	2.18	18.6	3.55	835	3.686
21.5	1.09	2.33	18.0	3.15	795	3.574
24.0	1.90	2.94	21.2	4.03	775	7.898
26.5	1.52	2.63	26.9	6.40	645	1.179
29.0	1.85	2.90	31.5	9.25	545	2.349
31.5	2.49	3.37	31.4	9.1	545	3.077
34.0	1.92	2.95	26.8	6.50	635	1.523
46.0	0.961	2.09	17.2	3.0	808	2.977
48.8	2.32	3.25	22.5	4.55	745	1.126
51.3	1.54	2.65	28.6	7.25	608	1.418
54.8	1.23	2.37	32.7	10.1	525	1.784
57.0	1.62	2.71	30.9	8.9	555	1.963
92.0	1.96	2.98	20.0	3.71	800	2.359
95.0	1.94	2.97	22.9	4.65	730	9.841
99.0	1.94	2.97	31.9	9.55	535	2.576
101	2.75	3.53	33.7	10.8	490	4.314
104	3.65	6.13	29.9	8.10	575	3.900
141	0.674	1.75	18.2	3.15	845	2.107
144	0.950	2.08	23.2	4.75	740	4.941
147	1.60	2.69	30.5	8.55	570	1.822
150	2.15	3.13	34.4	11.5	480	3.715
153	3.66	6.17	29.9	7.55	580	3.629

A: vapor pressure E-3 torr

Table 20. EXAMS-Calculated and Field-measured Flux for Molinate,
Normalized on Water concentration

TIME (hr)	EXAMS FLUX	FIELD FLUX	NORMALIZED[a] FIELD FLUX	RELATIVE[b] ERROR
0.75	21.1	17.2	15.6	-35.3
2	30.9	29.2	24.3	-27.2
3.3	32.3	25.9	19.3	-67.4
4.5	52.5	75.6	47.3	-11.0
5.75	61.9	91.3	50.7	-22.1
7	118.7	116.0	58.3	-103.6
8.25	106.6	92.5	95.6	-11.5
9.5	102.1	126	160.3	36.3
10.7	78.8	105	49.1	-60.5
12	36.6	46.2	21.0	-74.3
14	34.8	47.2	20.6	-68.9
16.5	29.4	44.7	18.6	-58.1
19	15.5	21.4	8.8	-76.1
21.5	15.0	18.0	7.5	-100.0
24.0	33.1	58.1	24.6	-34.6
26.5	49.5	25.7	11.4	-334.2
29.0	98.7	138	63.9	-54.5
31.5	129.2	154.0	74.4	-73.7
34	64.0	84.6	41.7	-53.5
46.0	12.5	12.8	6.8	-83.8
48.8	47.3	71.2	38.7	-22.2
51.3	59.6	53.7	29.5	-102.0
54.8	74.9	84.0	47.5	-57.7
57.0	82.5	64.9	37.3	-121.2
92	30.9	25.3	19.6	-57.7
95	41.3	36.3	28.8	-43.4
99	108.2	53.8	·44.5	-143.1
101	181.2	148.0	123.3	-47.0
104	163.8	198.0	167.8	2.4
141	8.85	8.25	8.3	-6.6
144	20.8	7.55	7.7	-170.1
147	76.5	25.8	26.9	-184.4
150	156.0	45.3	48.2	-223.7
153	152.4	69.0	75.0	-103.2

A: Field Flux normalized on water concentration. units are $ng/cm^2/hr*ppm$

B: Relative Error = $\dfrac{(Norm.\ Field\ Flux -- EXAMS\ Flux) \times 100}{Norm.\ Field\ Flux}$

COMPARISON OF PREDICTED AND FIELD FLUX

FLUX (ng/cm2/hr)/P.P.M.

TIME AFTER APPLICATION (hr)

EXAMS

FIELD

agreement between (Exams prediction and aerodynamic method) calculation observed for daily averages in the 1983 study (Seiber et al., 1986), but adds considerable detail in the diurnal fluctuations not available from the 1983 data.

Corresponding data for methyl parathion is in Tables 21 and 22, and in Figure 18. Agreement between the two profiles was generally evident, but not as good as for molinate. It should be noted that the largest disagreement was for fluxes at 14, 16.5, and 34 hours, where the field-measured flux far-exceeded the EXAMS prediction. These time periods were at midnite, 4:30 am, and 10:00 pm, respectively, when the field data for molinate flux indicated that volatilization should be close to minimal values. We thus feel that the disagreement at these three times (and perhaps others) was due to faulty field values (perhaps from air sample contamination) and that EXAMS-calculated values are closer to reality.

CONCLUSIONS

Molinate and methyl parathion underwent first order decline in rice field water, with approximate half-lives of 84 hrs (molinate, calculated from the time of maximum water concentration from dissolving granules which occurred at 17 hr after application) and 44 hr (methyl parathion, calculated from the concentration-time dissipation curve started 3 days after application). Dissipation of the two chemicals from water undoubtedly was due to a combination of hydrolysis, volatilization, microbial breakdown, photolysis and irreversible adsorption to sediments; volatilization was considered to be the major route for molinate based upon previous studies and the results of the jar experiment.

Table 21. Data for EXAMS Calculation of Volatilization Rate Constants for Methyl Parathion

TIME (hr.)	SOL PPM	VAPR E-6	WIND m/sec	KO2G	TCEL	RATE E-5
0.75	0.00	6.660	1.33	2.47	20.20	4.505
2.0	4.51	10.300	1.39	2.52	22.70	6.328
3.3	6.33	18.300	1.11	2.25	26.10	7.572
4.5	7.57	29.100	1.29	2.43	28.90	28.900
5.25	28.90	37.800	1.29	2.42	30.50	14.400
7.0	14.40	43.000	1.72	2.80	31.30	21.220
8.25	21.22	37.800	2.27	3.22	30.50	25.520
9.5	25.52	26.800	2.70	3.51	28.40	24.320
10.75	24.32	18.300	2.78	3.57	26.10	18.780
12.0	18.78	13.500	1.54	2.65	24.30	8.220
14.0	8.22	9.920	1.61	2.70	22.50	7.010
16.5	7.01	7.020	1.82	2.88	20.50	6.469
19.0	6.47	5.030	1.05	2.18	18.60	2.883
21.5	2.88	4.520	1.09	2.23	18.00	2.813
24.0	2.81	7.920	1.90	2.94	21.20	7.168
26.5	7.17	20.900	1.52	2.63	26.94	11.760
29.0	11.76	44.400	1.85	2.90	31.50	23.530
31.5	23.53	43.700	2.49	3.37	31.40	31.850
34.0	31.85	20.500	1.92	2.95	26.80	14.540
46.0	14.54	3.920	0.96	2.09	17.20	2.262
48.8	2.26	9.920	2.32	3.25	22.50	10.310
51.3	10.31	27.700	1.54	2.65	28.60	14.020
54.8	14.02	53.900	1.23	2.37	32.70	17.950
57.0	17.95	40.300	1.62	2.71	30.90	18.990
92.0	18.99	6.430	1.96	2.98	20.00	6.388
95.0	6.39	10.600	1.94	2.97	22.90	8.896
99.0	8.90	47.400	1.94	2.97	31.90	25.400
101.3	25.40	63.300	2.75	3.53	33.70	44.110
104.0	44.11	34.300	3.65	6.13	29.90	38.170
141.0	38.17	0.680	0.67	1.75	18.20	1.739
144.0	1.74	11.200	0.95	2.58	23.20	4.640
147.0	4.64	37.800	1.60	2.69	30.50	18.050
150.0	18.05	70.700	2.15	3.13	34.40	36.580
153.0	36.58	34.300	3.66	6.17	29.90	33.600

Table 22.   EXAMS Calculated and Field-measured Flux for
Methyl Parathion, Normalized on Water Concentration

TIME hr	EXAMS FLUX	FIELD FLUX	H2O CONC. PPM	NORM FLUX	RELATIVE ERROR
0.75	0.77	0.129	0.15	0.86	10.9
2.0	1.08	0.197	0.14	1.41	23.6
3.3	1.29	0.0	0.14	0.0	0.0
4.5	4.91	0.362	0.13	2.78	-76.4
5.25	2.45	0.297	0.13	2.28	-7.2
7	3.61	0.378	0.13	2.91	-24.1
8.25	4.34	0.749	0.125	5.99	27.6
9.5	4.13	0.732	0.12	6.10	32.2
10.75	3.19	0.492	0.12	4.10	22.1
12	1.40	0.265	0.12	2.21	36.7
14	1.19	0.823	0.118	6.97	82.9
16.5	1.10	0.546	0.115	4.75	76.8
19	0.49	0.116	0.11	1.05	53.5
21.5	0.48	0.187	0.105	1.78	73.1
24	1.22	0.105	0.105	1.00	-21.9
26.5	2.00	0.15	0.105	1.43	-39.9
29	4.00	0.555	0.103	5.39	25.8
31.5	5.41	0.767	0.1	7.67	29.4
34	2.47	0.814	0.08	10.18	75.7
46	0.38	0.0	0.07	0.00	0.0
48.8	1.75	0.168	0.07	2.40	27.0
51.3	2.38	0.217	0.065	3.34	28.6
54.8	3.05	0.0981	0.065	1.51	-102.2
57	3.23	0.184	0.055	3.35	3.5
92	1.09	0.0	0.055	0.00	0.0
95	1.51	0.0	0.055	0.00	0.0
99	4.32	0.0	0.055	0.00	0.0
101.3	7.50	0.0	0.055	0.00	0.0
104	6.49	0.0	0.055	0.00	0.0
141	0.30	0.0157	0.02	0.79	62.3
144	0.79	0.0263	0.02	1.32	40.0
147	3.07	0.0636	0.02	3.18	3.5
150	6.22	0.24	0.02	12.0	48.2
153	5.71	0.145	0.02	7.25	21.2

Figure 18. EXAMS-calculated (--) and Field-Measured Flux (o--o) of Methyl Parathion
vs Time.

FLUX FOR METHYL PARATHION

NORMALIZED FLUX (NG/CM2/HR/H2O CONC)

HOURS AFTER APPLICATION
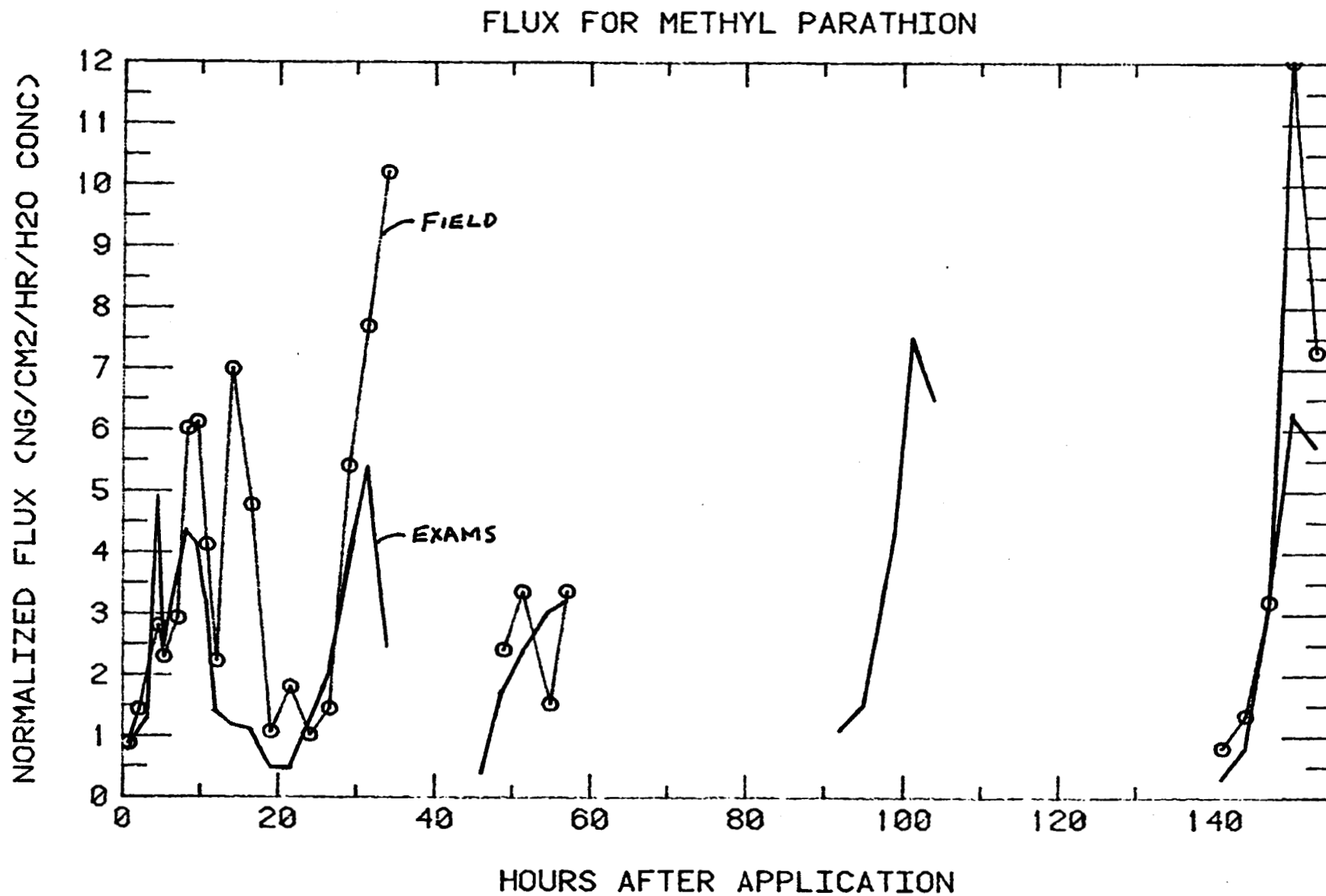
The volatilization route was assessed directly by conducting flux measurements at various intervals over a seven day holding period. The flux measurements gave very good data for molinate, reflecting the optimal fetch (exceeding the minimum 100:1 fetch-height ratio in nearly all cases), use of 6 measuring heights, and the availability of well calibrated meterological equipment. This shows the feasibility of gathering flux data above flooded agricultural fields -- the first time this has been demonstrated experimentally. The data for methyl parathion was also reasonably good, but somewhat more eratic because of the low air concentrations involved which were close to the analytical detection limits in many cases.

The measured molinate flux values led to an estimated volatilization rate of 0.082 kg/ha/12 hr day, or a loss of 0.58 kg (13% of the amount applied) in the seven day period. This is considerably lower then the estimated volatilization loss of 35% in a 4 day period after a 1983 application to the same field (Seiber et al., 1986). We believe that the 1983 result was higher in part because of higher molinate water concentration (due to an earlier application of molinate) and experimental error on the day of application which skewed the results to the high side. If this is so, then volatilization can account for only a part of the overall dissipation of molinate given the water concentration half-life of 3-4 days in this study. When the overall dissipation rate of molinate from rice field water was examined, it appeared that 45% should be lost in a 72 hr period (Table 23). The dissipation rate calculated from the jar experiment (no lids) roughly confirmed this, yielding a loss of 40% from water in a 72 hr period (Table 23). The jar experiment (closed) gave only 10% loss from water in 72 hr -- apparently the sum of all fate processes except volatilization and photodecomposition. Because photodecomposition was previously shown to be a minor fate process for

Table 23. Loss of Molinate From Water -- Summary

Source	% Lost in 72 hr Period
Dissipation From Field Water	45
Dissipation From Jar Water (open)	40
Dissipation From Jar Water (closed)	10
Aerodynamic Flux MEasurement	5-10
Microbial Metabolism	Negligable (Lit)
Hydrolysis	Negligable (Lit)
Soil Adsorption	<10 (Lit)
Photolysis	<10 (Lit)

molinate in rice field water (Soderquist et al 1977), it follows that 30-35% of the initial water content should be lost by volatilization in a 72 hr period. However, when the flux measurements were averaged, as discussed previously, only 5-10% loss by volatilization was actually obtained by the aerodynamic flux measurement (Table 23). One possibility is that chemical and/or microbial breakdown is more pronounced for molinate than estimated previously (Soderquist et al., 1977; Thomas and Holt, 1980); the results of the jar experiment, however, indicate that this is not so. Also, our own estimate of total volatilization based on flux measurements might be in error, because it does not include loss by this route in the late night and early morning hours (although the data show these to be periods of minimal volatilization), and it used daylight flux averages which were taken from data collected over just a fraction of the daylight hours available during the study period. This might explain part of the discrepancy but is not likely to explain all of it. The major explanation might well be that the aerodynamic method gave flux values lower than those actually occurring (see below).

For methyl parathion, volatilization flux was much lower (1/100th) than for molinate, but this must be tempered by the fact that the water concentration of methyl parathion was also much lower than for molinate. When flux is normalized on water concentration, the volatilization rate of methyl parathion was approximately 1/10th that of molinate -- a difference which is in keeping with the difference in Henry's law constant for the two chemicals (9.6×10^{-7} for molinate, and 10.3×10^{-8} m^3·atm/mole for methyl parathion). Apparently, volatilization is much less important than other dissipation routes for methyl parathion in paddy water. Because $t^{1/2}$ for methyl parathion in the water was just 44 hrs -- also much shorter than expected for chemical hydrolysis at the observed pH -- we tend to suspect that microbial or photochemical transformation was occurring for this chemical.

EXAMS was used to calculate volatilization flux for both chemicals, using field-measured values of temperature and wind speed (the primary variables affecting volatilization) and either experimental or estimated values of vapor pressure and water solubility at the field water temperatures. This introduced some uncertainty, particularly for molinate where the estimated water solubilities were made by extrapolating from data for another thiolcarbamate (EPTC). The EXAMS-calculated flux values, normalized on water concentrations, gave a profile over the sampling dates which correctly picked up all maxima and minima. The maximum fluxes from EXAMS were about twice those measured for 4 of the 5 maxima -- a situation which may have been due to errors in the estimation of water solubility which would have been most pronounced at the relatively high water temperatures corresponding to the maxima. Certainly, the temperature dependence of both water solubility and vapor pressure should be measured experimentally to clarify this. However, it is also possible that the EXAMS-calculated flux for molinate is closer to the real situation, and that the aerodynamic method for calculating flux from experimental meteorological and air concentration data is in error, on the low side. This situation could result from a molecular contribution to dispersion in moving air -- a factor which is more pronounced for relatively small molecules such as molinate (Glotfelty et al., 1983). It could also be due to the use of inappropriate factors in the aerodynamic calculation, casting some doubt on the validity of this method for measuring pesticide volatilization under any circumstance, not just from rice field water (Glotfelty, 1986).

For methyl parathion, EXAMS also correctly predicted the shape of the observed volatilization profile, particularly when 3 observed values were discounted as anomolously high due, apparently, to sampling and/or analytical errors.

Overall EXAMS appeared to be quite promising as a predictive tool for estimating volatilization loss from flooded rice fields. We believe that it may be useful for estimating loss from other dissipation routes as well, and for estimating overall dissipation from all routes -- a potentially useful capability for calculating rice water holding periods and perhaps other information needed to ensure safe use of pesticides in rice.

ACKNOWLEDGEMENTS

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